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Organic carbon accumulation in the South Atlantic Ocean: Sedimentary processes and glacial/interglacial budgets

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des Doktorgrades am
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Abstract

The accumulation of organic matter in marine sediments must be considered in order to estimate the magnitude of sources and sinks in the oceanic carbon cycle and of fluxes between the active reservoirs over timescales of 10^4 to 10^5 years. A significant change of global accumulation of organic matter (C_{org}) in marine sediments can therefore be responsible for changes in atmospheric carbon dioxide concentration over glacial-interglacial climate transitions. Past studies regarding this mechanism have focussed on high latitude oceans, particularly the Southern Ocean. There, no significant increases in C_{org} accumulation during the glacial could be observed. Little is known, in contrast, about basin-wide glacial to interglacial changes in C_{org} accumulation in the tropical and subtropical oceans.

The aim of this work was to contribute to the understanding of the importance of C_{org} accumulation in the global carbon cycle. For this purpose, modern spatial distribution of C_{org} accumulation was determined and quantified for the tropical and subtropical South Atlantic. Furthermore, sediment cores were used to reconstruct C_{org} accumulation rates for the Holocene and the Last Glacial Maximum (LGM). From the comparison of the two values, it was inferred whether and to what extent glacial accumulation of organic matter had increased over the entire study area. A general increase could have contributed to atmospheric CO_2 drawdown. A third field of study within this thesis concerned processes occurring between formation and deposition of organic matter in marine sediments and the time required for these processes.

Based on a compilation of surface sediment data generated within the frame of the Special Research Project 261 "The South Atlantic in the Late Quaternary" and of published data, modern C_{org} content in sediments from the tropical and subtropical South Atlantic was mapped. This map was combined with a map of Holocene sedimentation rates, which in turn is also based on new and published data, for a basin-wide budget of C_{org} accumulation. For the pelagic tropical and subtropical South Atlantic, annual accumulation of organic carbon was estimated at $1.8 * 10^6$ t C. From the maps it is evident that a large portion of total annual C_{org} accumulation occurs on the continental shelves and slopes along the continental margins. An accurate quantification of the amount of accumulation along the continental margins requires a high spatial resolution of the interpolation. From the coarse grid determined in this study for the basin-wide quantification, a conservative estimate of at least $1 * 10^6$ t C yr^{-1} for the shelves and slopes can be deduced. However, this value is probably too low, as small scale regional variability and steep gradients cannot be resolved in a coarse resolution grid. Therefore, a higher resolution study was carried out in

the Benguela coastal upwelling system, a high productivity system off Namibia. In this area, estimated annual C_{org} accumulation amounts to 2.5 * 10^6 t C, 2.15 * 10^6 t C of which are deposited on the shelf areas.

The regional distribution of organic rich sediments resembles the distribution of productivity in surface waters. However, in some areas, additional processes play a role. In the shallow areas on the continental shelf off Namibia for instance, sedimentation is influenced by current winnowing. Fine-grained organic rich sediments preferentially accumulate in morphologic depressions on the sea-floor. There, the fine-grained material is protected from currents, which prevents further resuspension. In the Eastern Equatorial Atlantic, effective remineralisation in the water column or at the sea-floor appears to be responsible for the small amount of organic matter that is deposited there in spite of high surface water productivity. Processes such as the above mentioned have to be taken into account when reconstructing paleoproductivity from the history of C_{org} accumulation in sediments.

In order to estimate basin-wide glacial changes in C_{org} deposition, accumulation rates of organic matter were reconstructed for the Holocene and the LGM using sediment cores. To avoid biasing towards higher values the Holocene accumulation rates referred to the time period from 8 to 4 ka before present. A bias could evolve when using data from surface sediments due to the fact that surface sediments are in diagenetic disequilibrium and are therefore relatively rich in organic matter. In the Benguela coastal upwelling system, a comparison of LGM and Holocene C_{org} accumulation rates implies that productivity was enhanced during the LGM. At the same time, upwelling cells were displaced seaward. Here, glacial-interglacial changes in total C_{org} accumulation changes are insignificant, as the deposition area on the shelf was greatly reduced due to the sea-level lowstand. Increased accumulation of organic matter during the LGM is observed almost everywhere along the continental margins and at many sites in the pelagic South Atlantic. This relative increase is large in the Eastern Equatorial Atlantic. However, this is the result of a combination of increased productivity and of better preservation of organic matter and possibly increased export efficiency. The reason for glacial decreases in C_{org} accumulation observed in some areas is not clear. On the outer Walvis Ridge, increased bottom current activity inducing stronger winnowing would be a possibility next to decreased productivity. At the Sierra Leone Rise north of the Equator, glacial productivity was probably slightly lower than during the Holocene.

The processes of re-suspension and re-deposition affect organic matter in particular and cause simultaneously deposited coarse-grained (calcareous) and fine-grained (organic)

particles to have different ages. This was shown using radiocarbon dating performed on planktic foraminifera and co-occurring alkenones, which are biomarkers synthesised by marine phytoplankton. Their respective radiocarbon ages differed on average by 2500 years with the organic biomarkers always being the older fraction. The average age difference can be regarded as a measure for the average residence time of organic matter in continuous re-suspension loops caused e.g. by internal tides. On the Namibian continental slope, tidal currents with velocities up to 25 cm/s were recorded at 1100 m water depth, 5 m above the sea floor. These currents cause re-suspension of organic aggregates from the sediment-water interface, while coarse-grained material remains deposited on the sea-floor.

The latter has important implications for the interpretation of paleoceanographic proxy data derived from alkenones or other substances residing in the fine sediment fraction. Age models, which are commonly based on analyses carried out on coarse grained sediment particles, may not be applicable for proxy records based on fine-grained material without correction. Furthermore, the signal recorded by carriers residing in the fine-fraction may have to be reinterpreted and considered a regional signal rather than a local one. The information derived from these proxy carriers depends on the possible source area of the allochthonous material. Apparent temporal offsets in multi-proxy studies can only be interpreted in a paleoceanographic sense, if confidence in the respective ages of the signal carriers is established.

The results of this thesis show that various processes occur between formation and deposition of organic material in the oceans, some of which may be active over several thousand years. Therefore it is problematic to associate observed patterns of accumulation with a certain point in time. Only a small portion of the total carbon cycling in the active reservoirs is removed for longer timescales ($>10^5$ years) from the ocean-atmosphere system via burial in sediments.

Zusammenfassung

Bei der Abschätzung der Größenordnung von Quellen und Senken im ozeanischen Kohlenstoffkreislauf sowie der Flussraten zwischen den unterschiedlichen Reservoirs, in der Atmosphäre, auf den Kontinenten und im Ozean, über Zeiträume von mehreren zehn- bis hunderttausend Jahren muss die Akkumulation von organischer Substanz (organischer Kohlenstoff = C_{org}) in marinen Sedimenten berücksichtigt werden. Für Änderungen im atmosphärischen Kohlendioxid-Gehalt im Zuge von glazial-interglazialen Klimawechseln kann deshalb auch eine signifikante Änderung der globalen C_{org}-Akkumulation im Ozean verantwortlich sein. In diesem Zusammenhang konzentrierten sich die Untersuchungen zur verbesserten Quantifizierung der Unterschiede zwischen glazialer und holozäner C_{org}-Akkumulation bisher meist auf Gebiete in hohen geographischen Breiten, insbesondere auf den Südozean. Dort konnten jedoch keine signifikanten Anstiege in der C_{org}-Akkumulation während der Glazialzeiten gegenüber den Interglazialzeiten nachgewiesen werden, die die niedrigen CO_2-Gehalte in der Atmosphäre während der Glazialzeiten erklären könnten. Flächenhafte Abschätzungen über glazial-interglaziale Änderungen in der C_{org}-Akkumulation in den tropischen und subtropischen Ozeangebieten sind bisher nur unzureichend erfolgt.

Ziel dieser Arbeit ist, die Bedeutung der Akkumulation organischer Substanz im Ozean für den globalen Kohlenstoffkreislauf besser abschätzen zu können. Zu diesem Zweck wurde die rezente C_{org}-Akkumulation im tropischen und subtropischen Südatlantik auskartiert und quantifiziert. Darüber hinaus wurden die für das Holozän und das Letzte Glaziale Maximum (LGM) rekonstruierten C_{org}-Akkumulationsraten aus Sedimentkernen verglichen. Hieraus wurden Rückschlüsse gezogen, ob und in welchem Maße die Akkumulation im Glazial flächenhaft zugenommen hat, wodurch erhöhte Mengen Kohlendioxids der Atmosphäre entzogen und im Sediment festgelegt worden sein könnten. Drittens sollte untersucht werden, welche Prozesse zwischen Bildung und Ablagerung von organischer Substanz stattfinden und innerhalb welcher Zeiträume sie wirken.

Anhand von Daten aus Oberflächensedimenten, die im Zuge der Arbeiten im Sonderforschungsbereich 261 „Der Südatlantik im Spätquartär" gewonnen wurden, und publizierten Werten wurde eine Karte der rezenten C_{org}-Gehalte in Sedimenten des tropischen und subtropischen Südatlantik erstellt. Diese wurde mit einer Karte von holozänen Sedimentationsraten, die ebenfalls auf eigenen und publizierten Daten basiert, kombiniert, um die flächenhafte Akkumulation von organischer Substanz abschätzen zu können. Sie beträgt im pelagischen tropischen und subtropischen Südatlantik etwa $1{,}8 * 10^6$

t C_{org} pro Jahr. Es wird deutlich, dass ein großer Teil des C_{org} an den Ozeanrändern auf den küstennahen Kontinentalhängen und -schelfen abgelagert wird. Mit einer groben räumlichen Auflösung bei der Interpolation von Sedimentdaten kann diese Menge jedoch nicht akkurat quantifiziert werden. Mit dem im Rahmen der Arbeit ermittelten groben Raster für den gesamten subtropischen und tropischen Südatlantik kann lediglich eine Mindestmenge von $1 * 10^6$ t C_{org} pro Jahr abgeschätzt werden. Dieser Wert ist wahrscheinlich viel zu niedrig, da durch Interpolation der Daten mit einer geringen räumlichen Auflösung kleinräumige Variationen und steile Gradienten nicht wiedergegeben werden. Deshalb wurde beispielhaft für das hochproduktive Benguela System, ein Küstenauftriebsgebiet vor Namibia, eine Untersuchung in größerer räumlicher Auflösung durchgeführt. Diese Untersuchung zeigte, dass dort jährlich etwa $2,5 * 10^6$ t C_{org} abgelagert werden, davon etwa $2,15 * 10^6$ t auf dem Schelf.

Die regionale Verteilung der Sedimente mit hohen C_{org}-Gehalten ähnelt der der Produktivität im Oberflächenwasser. Jedoch spielen in einzelnen Regionen auch andere Prozesse eine Rolle. In den flachen Schelfgebieten und am Kontinentalhang vor Namibia wird Sediment durch Bodenströmungen umgelagert. Dabei wird feinkörniges Material, in dem auch der größte Anteil der organischen Substanz enthalten ist, bevorzugt in morphologischen Senken am Meeresboden abgelagert. Dort ist der Strömungseinfluss so gering, dass die feinkörnigen Partikel nicht wieder in Suspension gelangen können. Im östlichen äquatorialen Atlantik scheint eine effektive Remineralisation in der Wassersäule oder am Meeresboden dafür zu sorgen, dass trotz erhöhter Produktivität im Oberflächenwasser verhältnismäßig wenig organische Substanz im Sediment abgelagert wird. Solche Prozesse müssen beachtet werden, wenn bei Abschätzungen für vergangene Zeiten aus den abgelagerten Mengen von organischer Substanz die Paläoproduktivität im Oberflächenwasser rekonstruiert werden soll.

Zur flächenhaften Abschätzung der relativen glazial-interglazialen Änderungen in der Akkumulation von organischer Substanz im Südatlantik wurden C_{org}-Akkumulationsraten für das LGM und für das Holozän ermittelt. Die holozänen Werte beziehen sich dabei auf den Zeitraum von 8 bis 4 tausend Jahren vor heute. Durch die Wahl dieses Zeitabschnitts sollte vermieden werden, dass bei der Verwendung von Oberflächensedimenten für die Bestimmung von C_{org}-Akkumulationsraten die Werte zu hoch eingeschätzt werden, da wegen noch unvollständiger diagenetischer Umsetzung der organischen Substanz an der Sedimentoberfläche die C_{org}-Gehalte dort relativ hoch sind. Im Benguela Küstenauftriebssystem deutet dieser Vergleich darauf hin, dass während des LGM die Produktivität erhöht war, zudem aber die Auftriebszellen wegen der

Meeresspiegelabsenkung seewärts verlagert waren. Allerdings wurde im LGM insgesamt nur unwesentlich mehr organischer Kohlenstoff abgelagert als im Holozän, da durch den niedrigen Meeresspiegelstand der Ablagerungsraum auf dem Schelf stark verringert war. Eine erhöhte Akkumulation von organischem Material während des LGM ist fast überall entlang der Kontinentalränder und an vielen Positionen im pelagischen Südatlantik zu beobachten. Im östlichen äquatorialen Atlantik ist der Anstieg im LGM mit einem Faktor 5 bis 6 relativ hoch, was jedoch nicht allein auf eine stark erhöhte Produktivität zurückzuführen ist sondern auch ein Resultat von besserer Erhaltung und erhöhter Exporteffizienz sein kann. In den Bereichen, in denen die glaziale Akkumulationsrate von organischer Substanz geringer ist als die holozäne Rate, ist die Ursache nicht bekannt. Auf dem äußeren Walvis-Rücken könnte neben herabgesetzter Produktivität auch eine erhöhte Erosion bzw. Resuspension von feinkörnigem Material wegen stärkerer Bodenströmungen im Glazial eine mögliche Erklärung sein. Am Sierra Leone-Rise nördlich des Äquators war die Produktivität im LGM wahrscheinlich geringfügig niedriger als im Holozän.

Die für den Kontinentalhang vor Namibia beschriebenen Umlagerungsprozesse, die vor allem die organische Substanz betreffen, führen auch dazu, dass gleichzeitig abgelagerte grobkörnige (karbonatische) und feinkörnige (organische) Partikel nicht das gleiche Alter haben. Dies wurde anhand von parallelen ^{14}C-Datierungen an planktischen Foraminiferen und Alkenonen (Biomarker, die von marinem Phytoplankton synthetisiert werden) gezeigt. Der Altersunterschied zwischen den Foraminiferen und den Alkenonen aus identischen Proben beträgt im Mittel etwa 2500 Jahre, wobei die Alkenone immer älter sind. Der Unterschied kann als ein Maß für die mittlere Verweilzeit von organischen Partikeln in Resuspensions-Schleifen am namibischen Kontinentalhang angesehen werden. Eine mögliche Ursache sind interne Tidenströmungen mit Geschwindigkeiten von bis zu 25 cm/s. Solche Strömungen konnten in Wassertiefen von ca. 1100 m, 5 m über dem Meeresgrund, gemessen werden. Diese Strömungen bringen feinkörnige, organische Aggregate auf der Sedimentoberfläche in Suspension, während grobkörniges Material liegen bleibt.

Für die Interpretation von paläozeanographischen Proxy-Daten, die durch Analysen von Alkenonen oder anderen Substanzen aus der feinkörnigen Sedimentfraktion gewonnen wurden, bedeutet diese Beobachtung, dass die für grobkörnige Sedimentpartikel ermittelte Alterskala nicht ohne Korrektur auf feinkörnige Partikel übertragen werden kann. Das Umweltsignal, das im feinkörnigen Material aufgezeichnet ist, muss zeitlich neu eingestuft und neu interpretiert werden, je nach der Herkunft des angelieferten Materials. In Multi-Proxy Studien können scheinbare zeitliche Versatze nicht paläozeanographisch interpretiert

werden, solange nicht sicher gestellt ist, dass die jeweiligen Partikelgruppen, an denen die Proxy-Parameter gemessen wurden, gleich alt sind.

Die Ergebnisse dieser Dissertation zeigen, dass zwischen der Bildung organischer Substanz und ihrer Ablagerung in Meeressedimenten vielfältige Prozesse stattfinden, die zum Teil mehrere tausend Jahre dauern können. Dies macht die zeitliche Zuordnung beobachteter Akkumulationsmuster problematisch. Insgesamt wird jedoch nur ein kleiner Anteil des gesamten Kohlenstoffs in den aktiven Reservoirs dem Atmosphäre-Ozean System durch die Ablagerung als organische Substanz im Sediment für längere Zeiträume ($>10^5$ Jahre) entzogen.

Introduction

1.1 Motivation and main objectives

One of the most prominent issues in Earth sciences is the understanding of the global carbon cycle. Changes in atmospheric concentrations of green-house gases are ultimately linked to fluxes of carbon as carbon dioxide (CO_2) and methane (CH_4) between the active carbon reservoirs.

The largest fluxes of the global carbon cycle are those that link atmospheric CO_2 to land vegetation and to the sea [*Schlesinger*, 1997]. On timescales of 10^4 – 10^5 years, accumulation of organic matter in marine sediments must be considered for estimates of the magnitude of sources and sinks in the oceanic carbon cycle and of the fluxes between the atmosphere, the continents and the oceans [*Berner*, 1982; *Hedges*, 1992; *Wollast*, 1998]. Significant changes in the global accumulation of organic matter in marine sediments can therefore partly account for changes in atmospheric CO_2 concentrations on glacial-interglacial timescales [*Broecker and Peng*, 1993]. However, until recently no detailed quantitative estimates of ocean-wide decreases or increases in organic carbon accumulation have been made.

In low latitudes, marine productivity is limited by nutrients such as phosphate and nitrate, while at high southern latitudes, these "macro-nutrients" are currently not completely consumed. There, other processes such as the supply of iron seem to be the limiting factors. Many studies have focused on the high-latitude oceans in order to investigate the amount of glacial-interglacial changes in productivity [*François et al.*, 1997; *Archer et al.*, 2000a; *Frank et al.*, 2000; *Moore et al.*, 2000; *Sigman and Boyle*, 2000]. Many of these studies suggest, however, that variations in productivity in the Southern Ocean are unlikely to have contributed to the major glacial atmospheric CO_2 drawdown [*Archer et al.*, 2000a; *Frank et al.*, 2000]. Instead, changes in deep water formation and water stratification are proposed to make a larger contribution to the lowering of atmospheric CO_2 concentrations [*François et al.*, 1997; *Archer et al.*, 2000a; *Moore et al.*, 2000; *Stephens and Keeling*, 2000].

In contrast, little is known about the contribution made by low- to intermediate latitude oceanic productivity. The South Atlantic is an example of a tropical to subtropical oceanic regime characterised by various high productivity environments. An equatorial upwelling system and one of the four large eastern boundary coastal upwelling systems of the world, the Benguela upwelling system, as well as frontal systems and vast areas of oligotrophic conditions can be studied in this ocean basin. Furthermore, deep water

formed in the Southern Ocean enters the South Atlantic as Antarctic Intermediate Water [*Reid*, 1989], and mixes with South Atlantic Central water. These water masses are upwelled in the Benguela system and originate directly from sources near the Subtropical Front. Therefore changes in intermediate and deep water circulation on glacial-interglacial timescales should affect the South Atlantic high productivity systems. Changes in primary productivity over glacial-interglacial have been investigated in various studies performed on individual sediment cores from some of the various productivity regimes [e.g., *Schneider et al.*, 1994, 1996, 1997; *Rühlemann et al.*, 1996; *Little et al.*, 1997a,b; *Schmiedl and Mackensen*, 1997; *Mulitza et al.*, 1998]. The amount of terrestrial organic matter that enters the South Atlantic via fluvial pathways is relatively well constrained [*Wagner and Dupont*, 1999; *Schlünz and Schneider*, 2000; *Schlünz et al.*, 2000] whereas the amount of marine organic matter accumulating in the deep South Atlantic is not well known.

Under present conditions, 80-90% of organic carbon accumulation occurs on the shelves [*Berner*, 1982; *Wollast*, 1998]. If these estimates are correct, glacial sea-level lowering must have resulted in a displacement of the major areas of deposition. Changes observed in organic carbon accumulation in coastal high productivity systems [e.g. *Schneider et al.*, 1996] would then not be exclusively due to changes in productivity, but would also result from such a displacement of depositional areas. As a consequence, the contribution to glacial lowering of atmospheric CO_2 made by increased biological productivity in coastal upwelling systems could have been over-estimated in past studies [e.g. *Sarnthein et al.*, 1988].

One goal of this thesis is to generate an improved estimate of organic carbon accumulation in the modern South Atlantic in relation to marine productivity by compiling all available data on organic carbon concentration and sedimentation rates. This compilation consists of the large data set from the special research project "The South Atlantic in the Late Quaternary" and published data. Regional trends in glacial to interglacial changes are investigated by comparing Last Glacial Maximum (LGM) and Holocene conditions (Chapter 2). The second goal was to achieve a more detailed organic carbon accumulation budget in the densely sampled Benguela coastal upwelling area during the Holocene and the LGM with special emphasis on the role of the shelf. This study revealed that the overall glacial increases in C_{org}-accumulation are relatively small (Chapter 3). A major result of this work is that in the Benguela system, sedimentation of organic matter is not only dependent on productivity patterns but is also influenced by the highly heterogeneous morphology of the depositional area and related patterns of bottom water currents. These processes result in different sedimentological behaviour of different

sedimentary grain sizes. Therefore the third objective was defined as a detailed assessment of sedimentation processes affecting different grain-size fractions in this highly dynamic upwelling system, and the temporal relationship of proxy parameters derived from these grain-size fraction. This was carried out using absolute radiocarbon dating techniques and is discussed in Chapter 4. The results of this study imply that due to sedimentary processes such as re-suspension, organic particles may remain near the sediment-water interface for several thousand years until they are finally buried.

1.2. The carbon cycle

1.2.1 Global carbon reservoirs

Most of the carbon on Earth is stored either in carbonate rocks or in kerogen and does not take part in dynamic exchange processes between the atmosphere and the oceans [*Schlesinger*, 1997]. The fraction of the total carbon on the Earth that undergoes active biogeochemically mediated exchange processes is relatively small [*Hedges*, 1992]. Of the active reservoirs, the pool of dissolved inorganic carbon (DIC) in seawater is by far the largest [*Siegenthaler and Sarmiento*, 1993]. Most of this is stored in the deep ocean, while the size of the warm surface ocean reservoir is comparable to that of the atmosphere. The major fluxes between the active reservoirs, i.e. the terrestrial biosphere, soils, the atmosphere, the ocean and marine sediments, are illustrated in Figure 2.1.

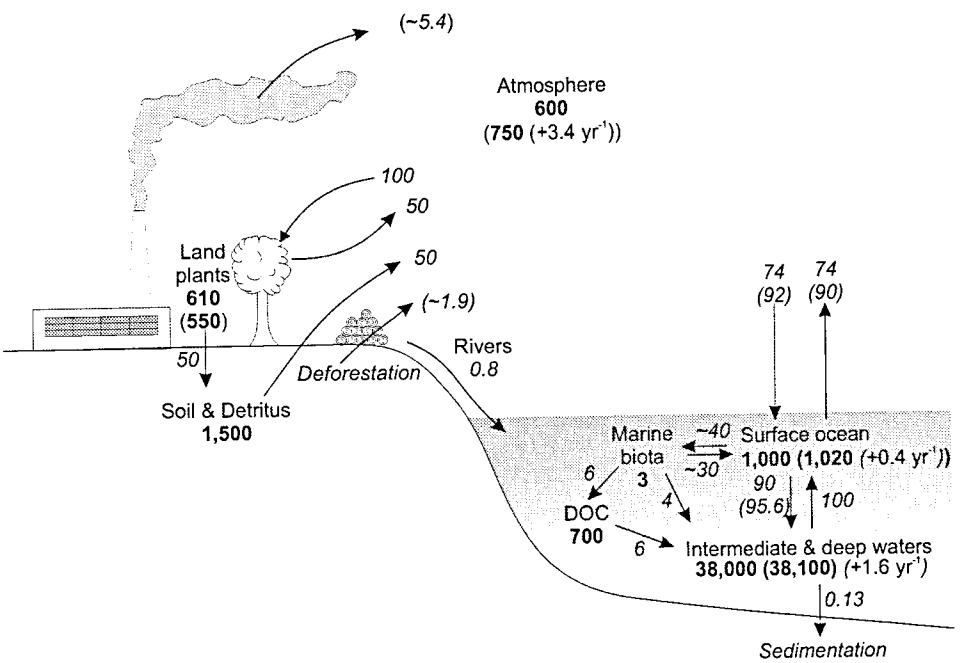

Figure 1.1. The global carbon cycle. All pools are expressed in units of 10^{15} g C (10^{15} g = Gt =Pg). Fluxes are given in italic font and expressed in units of 10^{15} g C yr^{-1}. Figures in parentheses are values after anthropogenic perturbation. Modified after *Siegenthaler and Sarmiento* [1993]

Most of the Earth's organic matter is generated by photosynthetic fixation of inorganic carbon by terrestrial plants and marine phytoplankton from atmospheric CO_2 and surface-ocean dissolved inorganic carbon (DIC) respectively. Through subsequent transformation and degradation of the organic fraction in soils and marine sediments, dissolved organic carbon (DOC), and respired CO_2 are formed. Net global primary production on land is estimated at approximately 50-60 Gt C yr^{-1} (50 Gt in Figure 1.1) [*Hedges*, 1992], and estimates of marine global primary production are on the order of 36-46 Gt C yr^{-1} (40 Gt in Figure 1.1) [*Antoine et al.*, 1996; *Behrenfeld and Falkowski*, 1997]. Efficient terrestrial and marine heterotrophic degradation allows less than 1 % of the total primary production to be preserved [*Berger et al.*, 1989]. Much of the organic matter deposited in soils on land is eventually eroded and transported to the ocean by rivers. The total annual burial of organic carbon in marine sediments is estimated at approximately 126 * 10^{12} g C [*Berner*, 1982]. More than 80% of this is believed to take place on the continental shelves [*Berner*, 1982, *Wollast*, 1998], which serve also as primary repositories of organic carbon derived from terrestrial sources. However, the fate of most of the terrestrial organic matter discharged to the sea by rivers remains enigmatic, as only a small fraction of the organic matter dissolved in seawater and preserved in marine sediments appears to be land-derived [*Hedges et al.*, 1997]. In contrast to soils, marine sediments are a relatively closed and persistent reservoir, which is not affected much by processes such as weathering [*Hedges and Oades*, 1997]. Marine sediments generally remain undisturbed over several million years and eventually undergo lithogenesis. Organic matter deposited on the sea-floor may become a source material for oil formation. Thus the most important longer term sink of carbon out of the active reservoirs is by burial in marine sediments. Changes in the amount of organic matter that is annually buried on the sea-floor may potentially have an important influence on the carbon concentration in the active reservoirs such as the atmosphere.

1.2.2 Variations in atmospheric carbon dioxide

As a result of human activity such as fossil fuel burning and deforestation, fluxes between the active carbon reservoirs have changed. Annually, approximately 5-6 Pg (= 5-6 Gt) of carbon is released to the atmosphere by these human activities. However, atmospheric CO_2 concentrations do not increase at the same rate. The fate of much of the anthropogenically released carbon is unclear, and much research effort is directed towards the search for the "missing sink". Anthropogenic perturbations of the global carbon cycle, however, are not addressed in this thesis. Instead the study is concerned with the better

understanding of the marine carbon cycle, which has been pursued by investigation of past variations at different climatic stages.

Measurements of gas bubbles trapped in ice cores revealed that the atmospheric concentration of CO_2 has fluctuated between 190-200 ppmV during glacial and approximately 280 ppmV during interglacial periods [e.g. *Barnola et al.*, 1987; *Petit et al.*, 1999]. The very regular pattern of these variations suggests that a well-ordered set of dominant mechanisms is responsible. As yet, there is no broadly accepted explanation for this difference and its recurrence on a 100 kyr cycle. As stated above, the largest active reservoir of carbon is the deep ocean storage of inorganic carbon. Deep water is exposed to the ocean surface roughly every 1000 years, so that a change in atmospheric CO_2 driven by something other than oceanic processes would be diluted into the large reservoir of deep ocean DIC. Hence the driving mechanism is thought to be a marine process.

Among the oceanic mechanisms that have been suggested to explain the glacial-interglacial variations of atmospheric CO_2 are: a) An increase in biological productivity in surface waters and subsequent export of the organic matter to the deep sea. This biological pump, could account for the glacial drawdown of CO_2 in the atmosphere [*Broecker and Peng*, 1986]. b) Changes in the carbonate system of the seawater could lead to storage of more carbon in the dissolved inorganic pool [*Archer and Maier-Reimer*, 1994]. Such a change in the inorganic carbon pool of the seawater would require the calcite lysocline to have been deeper during the glacials in order to cause a drawdown of atmospheric CO_2. c)The "physical pump" describes the flux of CO_2 to depth driven by the downward mixing of water associated with the formation of deep-water masses, but also the upwelling of cold, CO_2-rich deep-water to the surface and subsequent outgassing. d) The solubility of CO_2 in water increases with decreasing temperatures. During the glacials with surface waters being colder than at present, high latitude export of dissolved CO_2 to the deep ocean could therefore have been increased, and outgassing at low latitudes would have been reduced. This process is referred to as the "solubility pump". None of the hypotheses proposed have been able to explain all of the observations [*Archer et al.*, 2000b], and modelling efforts have focused on high latitudes [*Sigman and Boyle*, 2000].

1.2.3 The biological pump

The term "biological pump" refers to the process by which carbon fixed by photosynthetic activity is exported to the deep sea. During the downward passage of the exported particles, a large proportion of the organic matter is oxidised, releasing CO_2 into the sub-surface waters, while a minor fraction of organic carbon is stored in the sediments.

This is why the partial pressure of carbon dioxide (pCO_2) in surface water is lower than pCO_2 of deep water masses. If the efficiency of the biological pump increases, more CO_2 is removed from surface waters. Equilibration of the CO_2-depleted surface water with the atmosphere will eventually result in a decrease of atmospheric CO_2 concentration.

Some researchers surmise that the whole-ocean reservoir of nutrients fostering primary production was larger during the glacial times, strengthening the biological pump at low latitudes, where these nutrients are currently limiting [*Broecker*, 1982; *Broecker and Henderson*, 1998]. Quantitative assessments of the actual amount of organic carbon deposited on the sea-floor at present are scarce [e.g. *Berner*, 1982], and only rough estimates exist for the glacials [e.g. *Sarnthein et al.*, 1988]. Modelling results suggest that glacial levels of atmospheric CO_2 could be attained if low latitude production during the glacial was increased by 50% with respect to the modern value [*Sigman et al*, 1998].

An important aspect when discussing changes in low latitude production over glacial/interglacial timescales is the effect it has on the carbonate chemistry of the ocean. The absolute amount of organic carbon exported to the deep sea is not the only relevant factor with respect to the carbon cycle. Low latitude export production also determines the amount of calcium carbonate that is exported to the deep sea. The amount of carbonate deposited on the sea-floor balances the input of alkalinity by rivers, and this balance is maintained by the distribution of calcite burial in the deep sea. This distribution is mediated by the depth of the calcite lysocline. The area of the sea-floor where calcite is deposited is larger at times of increased input of alkalinity, in turn causing atmospheric CO_2 to decrease. However, investigations of glacial lysocline depths have revealed that on average they are not significantly different than during the Holocene [*Catubig et al.*, 1998].

The relative proportions of carbonate and organic matter in the sinking particles have an important influence on alkalinity as well. Decreasing the rain ratio of carbonate to organic matter will cause a decrease in atmospheric CO_2, partly by enhancing CO_2 solubility in surface waters and partly by decreasing deep-sea carbonate burial [*Sigman and Boyle*, 2000]. This could be an explanation why no significant deepening of the lysocline during the LGM is observed, as would be expected if the mechanism causing atmospheric CO_2 drawdown were ultimately linked to the inorganic carbon cycle. Such a change in rain ratio coupled with increases in productivity could produce glacial atmospheric levels of CO_2 [*Sigman and Boyle*, 2000].

In order to investigate possible mechanisms accounting for glacial atmospheric CO_2 levels, calcite burial in the deep ocean has been mapped for the Holocene [*Archer*, 1996] and compared with the glacial distribution [*Catubig et al.*, 1998]. Changes in deep water

alkalinity are hard to assess, and only few estimates of glacial deep-ocean pH exist [*Sanyal et al.*, 1995, 1999, 2001]. Changes in organic matter burial, in contrast, should be easy to measure when looking at the amount of organic carbon accumulating in deep sea sediments at the respective times. Detailed estimates of modern and past organic carbon burial in deep-sea sediments may help quantify the role of the biological pump in the global carbon cycle. This thesis attempts to estimate modern organic carbon accumulation in the tropical and subtropical South Atlantic (Chapter 2), as well as for the Holocene and the LGM in the Benguela upwelling system (Chapter 3).

1.2.4 Processes affecting carbon burial

The amount of carbon buried in deep-sea sediments is dependent on several factors, the most prominent one being the amount of photosynthetically fixed carbon produced in and subsequently exported below the euphotic zone. Continuous degradation of the exported organic particles during their passage through the water column leads to the observed distribution of large fluxes to the sea-floor in shallow water environments and small fluxes to the deep-sea floor [e.g. *Wollast*, 1998]. Consequently equations to relate the C_{org} export to a specific water depth have been proposed [*Suess*, 1980; *Betzer et al.*, 1984]. Changes in accumulation rate of organic carbon on glacial-interglacial timescales have been attributed to changes in productivity, and observed accumulation rates of organic carbon have been used to reconstruct paleoproductivity based on empirical equations [*Müller and Suess*, 1979; *Stein*, 1986; *Sarnthein et al.*, 1992].

However, there is evidence that export to a certain depth and thus the potential for organic carbon accumulation in the sediment may be site or region specific [*Berger and Wefer*, 1990; *Wefer and Fischer*, 1993; *Fischer and Wefer*, 1996; *Fischer et al.*, 2000; *Antia et al.*, 2001]. Moreover, a particle's settling velocity and the reaction rates of the compounds determine the extent of organic matter degradation within the water column [e.g., *Armstrong et al.*, 2002]. There is increasing evidence that organic matter is protected from degradation by the inorganic matrix of the sinking particles [*Hedges et al.*, 2001], and that the flux of ballast minerals such as dust or biominerals determine deep-water organic carbon fluxes [*Armstrong et al.*, 2002].

Lateral transport of organic particles during settling or by resuspension in nepheloid layers influences the amount and location of deposition of organic matter [e.g. *Lampitt et al.*, 1995; *Thomsen and van Weering*, 1998; *Freudenthal et al.*, 2001]. These transport processes are particularly important at continental margins, and export of organic matter from the shelves to the slopes and the adjacent deep sea basins accounts for significant fractions of

total fluxes [*Biscaye and Anderson*, 1994; *Hall and McCave*, 1998; *Bauer et al.*, 2001]. It is not clear, however, how much time passes between formation of organic particles and final burial in sediments on the slope or in deep-sea basins. Chapter 4 of this thesis addresses this problem.

After deposition on the sea-floor, degradation of organic matter continues. Organic matter is the primary energy source for macrobenthic and microbial life. Among the factors controlling preservation of organic matter in the sediments are the sedimentation rate, bottom water oxygen concentration, the surface area of mineral grains, the oxygen penetration into the sediment, oxygen exposure time and the molecular composition of the material [*Müller et al.*, 1988; *Canfield*, 1994; *Mayer*, 1994; *Hedges and Keil*, 1995; *Hartnett et al.*, 1998]. As a result, organic carbon is not a reliable proxy for paleoproductivity in many areas of the oceans, particularly in oligotrophic regions [*Rühlemann et al.*, 1999].

Many of the parameters affecting organic carbon burial may vary over glacial-interglacial timescales. Furthermore, sites of high productivity may be at different locations during different climatic states. Particularly in coastal upwelling systems, near shore high productivity cells will migrate seaward in response to sea-level lowstands. Therefore, glacial-interglacial changes in organic carbon accumulation at a specific site may not only be the result of general changes in productivity, but instead may also reflect different hydrographical or sedimentological conditions (see Chapters 2, 3 and 4). Regional maps of organic carbon concentration and accumulation for glacial and interglacial times can help in the understanding of processes leading to the features observed at individual sites.

1.3 Stratigraphic control and the quantification of organic carbon accumulation

The most important prerequisite for studies on glacial-interglacial timescales is a reliable stratigraphic control of the sediments investigated. Only if confidence is provided that sediment records are precisely dated, interpretation of the data can yield valid results and comparison between cores is feasible. Correlation of neighbouring sediment cores is a straightforward method and can be performed based on various sedimentary parameters, assuming that lateral variations in sedimentary characteristics are smaller than variations in sediment thickness. Examples for sediment properties used for core-to-core correlation are carbonate concentration [e.g. *Jansen et al.*, 1996], sediment colour [*Chapman and Shackleton*, 1998], or magnetic susceptibility [*von Dobeneck and Schmieder*, 1999; *Schmieder et al.*, 2000].

The most widely used method to date individual deep sea cores is stable oxygen isotope stratigraphy. This method is defined by the variation in the ratio of the two stable oxygen isotopes (^{18}O and ^{16}O) in seawater over glacial-interglacial timescales. During

glacials, ocean waters are relatively enriched in the heavier isotope ^{18}O, as water containing the lighter isotope ^{16}O is preferentially evaporated and consequently fixed in continental ice. The stable oxygen isotope ratio of sea-water is recorded in the carbonate shells of marine organisms that can be picked from the sediments. The shells of foraminifera or other planktic or benthic organisms are most commonly used for this purpose. The down-core variations in this ratio are visually matched with dated standard curves [*Imbrie et al.*, 1984; *Martinson et al.*, 1987]. However, the temporal resolution of these standard curves is limited and the error in dating single events of this oxygen isotope stratigraphy amounts to an average range of ±2.5 kyrs [*Martinson et al.*, 1987].

Estimates of organic carbon accumulation are made by calculating an accumulation rate as a product of organic carbon concentration in the sediment, dry bulk density and sedimentation rates derived from the age model for the respective cores. As sedimentation rates represent average values over core intervals between dated core depths, abrupt changes in sediment characteristics and rapid, short duration sedimentation events cannot be resolved by this method. Furthermore, increased or decreased accumulation at a certain site as a result of bottom current winnowing can produce overestimates of regional sedimentation rates, as cores are preferentially taken at sites of increased accumulation. These errors have therefore put further limitations on the organic carbon based method of reconstructing productivity, in addition to potential diagenetic alteration of the organic carbon signal on the sea-floor.

Accumulation rates derived from oxygen isotope stratigraphy can be corrected and refined by studying $^{230}Th_{ex}$ fluxes. The application of the $^{230}Th_{ex}$ method can serve as a tool to identify sections of redistributed sediments and offers the possibility to quantify the amounts of laterally supplied material [see: *Frank et al.*, 1999, for a review]. The method is based on the uniform distribution of ^{230}Th produced in the water column by radiodecay of uranium. The high particle reactivity of ^{230}Th causes a very low residence time of only 5-40 years in the water column. As a result, dissolved ^{230}Th can not be transported over significant distances. Instead, the flux of ^{230}Th into the sediment is assumed to match its local production rate. Deviations from the expected values occur when lateral sediment redistribution has been active. Furthermore, ^{230}Th rain rates can be used to correct for stratigraphic uncertainties in oxygen isotope dated cores. ^{230}Th profiles in sediment cores from the Benguela upwelling system imply focussing of organic rich material [S. Reuter and A. Mangini, Heidelberger Akademie der Wissenschaften, personal communication]. The temporal resolution of ^{230}Th correction factors, however, remains a function of the stratigraphic tie points.

For higher temporal resolution, absolute dating methods need to be applied. For studies of the late Pleistocene, radiocarbon dating is the most established method for precise age determination.

1.3.1 Principles of radiocarbon dating

In the following, background information on radiocarbon dating, which is frequently applied in paleoceanographic studies, is provided. For the study presented in Chapter 4 the technique was applied, but basic information on the conventional reporting is given here in order to facilitate a concise discussion of the data in Chapter 4. Carbon occurs in three natural isotopes, with atomic weights of 12 (98.9%), 13 (1.1%) and 14. The isotope with an atomic weight of 14 (^{14}C) is radioactive and is therefore commonly referred to as radiocarbon. Radiocarbon is produced in the upper atmosphere by collision of cosmic ray neutrons with nitrogen (^{14}N), emitting a proton (H). The ^{14}C is rapidly incorporated into atmospheric CO_2 and takes part in the active carbon cycle. Approximately $1/10^{12}$ of the total atmospheric CO_2 contains a radioactive carbon atom.

The distribution of the heavier carbon isotopes (^{13}C and ^{14}C) between the carbon reservoirs is affected by thermodynamic and kinetic fractionation processes. These effects are rather well known for the stable isotope ^{13}C. Ratios between ^{13}C and ^{12}C are reported as $\delta^{13}C$ in per mil (‰) relative to a standard. Fractionation effects between two substances A and B ($\varepsilon_{A/B}$) can be approximated by the difference between their measured $\delta^{13}C$ values. $\varepsilon_{A/B}$ associated with equilibrium reactions such as inorganic speciation in sea-water are in the range of 1 to 10‰ [*Hayes*, 1993, 2001]. Biologically mediated carbon transfers, e.g. photosynthetic carbon fixation, involve large $\varepsilon_{A/B}$. Typical values for enzymatic fractionation of ^{13}C range from -18 to -29‰, but fractionation of up to -60‰ occurs in natural systems [*Hayes*, 2001]. Isotopic fractionation affects radiocarbon approximately twice as strongly as ^{13}C. Hence fractionation effects have to be considered when using the radiocarbon dating method (see below).

Radiocarbon decays to nitrogen by emission of β-rays with a half-life of 5730 years. This process is used to determine the true age of a sample by measuring its radiocarbon activity, which has to be corrected for isotopic fractionation. For the determination of radiocarbon ages, a number of agreements and definitions are made. In the following, a summary of these conventions is given, which is based on the equations by *Stuiver and Polach* [1977].

The absolute international standard ^{14}C activity (A_{abs}) is defined as 95% of the activity of the original oxalic acid standard in the year 1950 normalized to a defined $\delta^{13}C_{ox}$ value of

-19‰. This defined activity does not change, although the activity of the oxalic acid standard that is actually measured does change. The measured activity of the original oxalic acid standard (A_{ox}) is corrected for isotopic fractionation:

(1) $$A_{on} = 0.95\, A_{ox}\{1-[2(19+\delta^{13}C)/1000]\}.$$

The fractionation normalized value A_{on} is subsequently corrected for the decay between 1950 and the year (y) of the measurement to yield the absolute international standard activity:

(2) $$A_{abs} = A_{on}e^{\lambda(y-1950)}$$

where λ equals $1/8267\ yr^{-1}$, which is the true decay constant. A_{abs} is defined as zero on the radiocarbon age timescale, thus an age of zero ^{14}C-years always corresponds to the year 1950.

The measured radiocarbon activity of a sample (A_s) is normalized to a constant $\delta^{13}C$ of -25‰ (A_{sn})

(3) $$A_{sn} = A_s\{1-[2(25+\delta^{13}C_{sample})/1000]\}$$

in order to remove the influence of isotopic fractionation and to make ages obtained from different substances comparable.

Modern radiocarbon measurements are performed using an Accelerator Mass Spectrometer (AMS) device, which does not measure the rate of ^{14}C decay but rather the absolute ratios of ^{14}C to ^{12}C in a sample ($R^{14/12}$). AMS ^{14}C data are reported as fraction modern (fMC) values:

(4) $$fMC = A_{sn}/A_{on} = R^{14/12}{}_{sn}/\ R^{14/12}{}_{ON}$$

or as percent modern (pMC):

(5) $$pMC = 100\ fMC.$$

From these expressions, a radiocarbon age can be calculated assuming a constant time-independent atmospheric ^{14}C level in all past times. The activity or radiocarbon concentration of this hypothetical atmospheric level after normalization to a $\delta^{13}C$ of -25‰ is by definition equal to A_{abs}. In the literature, radiocarbon ages are commonly reported as "conventional radiocarbon ages". The conventional radiocarbon age (t) in years before 1950, referred to as before present (BP), is:

(6) $$t = -8033 \ln A_{sn}/A_{on}.$$

It is important to note that for the calculation of these conventional radiocarbon ages, the so called "Libby halflife" of 5568 years is used in order to maintain comparability of all published radiocarbon ages, regardless of further corrections of the precise halflife of radiocarbon.

When a radiocarbon age as a year date before present is not desired, data are reported as $\Delta^{14}C$:

$$\Delta^{14}C = 1000\,[A_{sn}/A_{abs}-1] \quad (7)$$

If the year of sample formation is known, a correction for the decay between the formation and measurement can be applied. In this thesis, only samples of unknown age were analysed.

1.3.2 Atmospheric radiocarbon variability and calendar ages

In a first approach it has been assumed that the atmospheric ^{14}C level has been constant in all past times within the range of the method (i.e. ~50,000 years before present). It is now recognized that the atmospheric $^{14}C/^{12}C$ ratio has not been stable during the past (Figure 1.2). This is deduced from observed discrepancies between conventional radiocarbon ages of tree rings or varved lake sediments and their "directly dated", i.e. counted, ages [see e.g. *Stuiver et al.*, 1986; *Stuiver et al.*, 1986; *Kromer and Becker*, 1993; *Pearson et al.*, 1993; *Stuiver and Pearson*, 1993; *Stuiver and Reimer*, 1993; *Goslar et al.*, 1995a]. Further evidence is provided by comparison of U-Th and ^{14}C dating of coral reefs [*Bard et al.*, 1990] and from comparison of ice core and marine records [*Voelker et al.*, 1998].

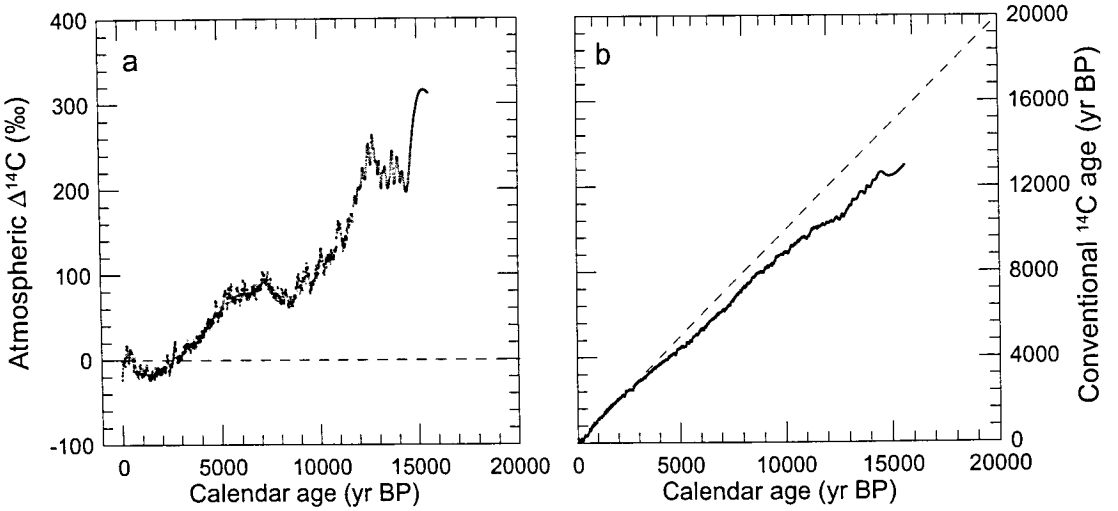

Figure 1.2. Variations of atmospheric radiocarbon concentration over the past 15,000 years (a); deviation of conventional radiocarbon age from calendar years (b) (data from Stuiver et al., 1998a).

In order to determine the true age of a sample, conventional radiocarbon ages therefore have to be calibrated to calendar years. This is commonly done by using the public domain software CALIB [*Stuiver et al.*, 1986; *Stuiver and Reimer*, 1993; *Stuiver et al.*, 1998b]. The most recent version 4.2 is available at http://depts.washington.edu/qil/calib/.

The temporal variation of the atmospheric $^{14}C/^{12}C$ ratio is linked to changes in the dipole intensity of the Earth's magnetic field [*Mazaud et al.*, 1991; *Laj et al.*, 1996], solar activity [e.g. *Bond et al.*, 2001; *Kromer et al.*, 2001] and ocean circulation [e.g. *Goslar et al.*, 1995b; *Hughen et al.*, 2000]. The former two processes are external and affect the production of radiocarbon in the atmosphere. They are active on century timescales (solar activity) and cause long-term trends (intensity of the magnetic dipole). Changes in oceanic circulation affect the atmospheric radiocarbon concentrations due to internal changes in the Earth's carbon cycle. An overview of radiocarbon calibration is given by *Bard* [1998].

The amount of atmospheric radiocarbon nearly doubled in response to nuclear weapon testing in the 1950s and 1960s [*Levin et al.*, 1985; *Levin and Kromer*, 1997]. Following the stop of above-ground weapon testing in 1962, the excess radiocarbon has been taken up by the terrestrial and marine carbon reservoirs. It serves as a useful tracer of carbon pathways through the reservoirs and oceanic turnover [e.g. *Broecker et al.*, 1985; *Severinghaus et al.*, 1996]. Materials that have taken up some of this bomb-radiocarbon have a $\Delta^{14}C$ value >0‰.

An additional, but much smaller anthropogenic influence on atmospheric ^{14}C concentration is related to fossil fuel burning [*Suess*, 1955]. Fossil fuel does not contain any radiocarbon, and the CO_2 that is produced by its combustion lowers the natural atmospheric radiocarbon concentration.

1.3.3 Distribution of radiocarbon in the carbon reservoirs

After production in the atmosphere, $^{14}CO_2$ is fixed by photosynthetic processes and rapidly distributed throughout the active carbon reservoirs. Carbon in living plant and animal biomass is therefore assumed to be in equilibrium with the atmosphere's radiocarbon content. This, however, is only true as a first approximation and special cases must be considered. If an organism assimilates a fraction of pre-aged carbon, for example animals that feed on soil humus, an appropriate radiocarbon age of this organism can only be calculated after the assimilation of this component is corrected for. This is achieved by subtracting the appropriate "reservoir age", i.e. the age of the carbon source utilized by the organism relative to the age of the atmosphere. Bacteria feeding on oil spills are an obvious example. Fossil fuel does not contain measurable amounts of radiocarbon, it is "radiocarbon dead". Even living bacterial biomass will therefore contain carbon of infinite age ($\Delta^{14}C$ = -1000‰). This effect has recently been used as evidence for bacterial assimilation of organic material from shales during weathering [*Petsch et al.*, 2001].

In the marine system, a further complication arises from the fact that no oceanic carbon pool begins with an "age" of zero years. This is the result of the time required for distribution of the isotopes between the dissolved inorganic carbon (DIC) species, i.e. CO_{2aq}, HCO_3^-, and CO_3^{2-}, which keeps $DI^{14}C$ out of equilibrium with the atmosphere by radiodecay occurring simultaneous with the process of DIC speciation. A second process is upwelling of deep-ocean water to near the surface, where it mixes with waters in contact with the atmosphere. The DIC in this upwelled water has been removed from contact with the atmosphere for up to 1500 years, during which significant amounts of radiocarbon have decayed. Downwelling of water at other sites removes surface water from contact with the atmosphere. A steady state balance between the input of radiocarbon from the atmosphere and its removal by advection and radiodecay in the water column is maintained. The age difference between the atmosphere and the surface ocean is termed the "reservoir age" of surface water [e.g., *Stuiver and Polach*, 1977; *Bard*, 1988].

At present, the reservoir age of surface waters in the ocean varies between 300 and 1200 years, mainly as a function of oceanographic setting [*Bard*, 1988]. High latitude surface waters are old because of upwelling of subsurface water. At latitudes between 40°N and 40°S, surface water reservoir ages are approximately 400 years [*Bard*, 1988], except in upwelling areas [e.g. *Southon et al.*, 1990]. Due to the anthropogenic perturbations of natural radiocarbon concentrations, however, it is not possible to measure natural reservoir ages directly [*Bard*, 1988; *Broecker et al.*, 1995]. Instead, reservoir ages are reconstructed from samples collected before 1950, or modelled using assumptions on physical parameters of the ocean [*Bard*, 1988].

In response to changes in ocean ventilation, the reservoir ages of surface waters have varied over time [*Bard*, 1988; *Goslar et al.*, 1995b; *Bard*, 1998; *Hughen et al.*, 2000; *Waelbroeck et al.*, 2001]. Reservoir ages in higher latitudes are particularly sensitive to changes in ocean circulation [*Bard*, 1988, 1998; *Waelbroeck et al.*, 2001]. Sparse data on past reservoir ages exist, where contemporaneous samples from marine and terrestrial environments associated with the same volcanic ash layer were dated [e.g. *Siani et al.*, 2001]. Regionally different changes in past reservoir age are a potential pitfall when studying the relative timing of radiocarbon dated marine records from different areas. Past changes of reservoir age are often linked to the intensity of upwelling and the source area of upwelled waters. These processes are hard to assess in themselves. Therefore, little is known about surface water reservoir ages in upwelling areas. As a consequence no reservoir age corrections are applied to radiocarbon ages from the Benguela upwelling area studied in this thesis (Chapter 4).

1.3.4 Radiocarbon dating in marine sediments

In principle, all materials containing carbon can be used for radiocarbon dating. In marine sediments, either carbonates or the organic fraction are commonly chosen. Carbonate shells are abundant in marine sediments. These shells are produced by phytoplankton (e.g. coccolithophorids or dinoflagellates), zooplankton (e.g. planktic foraminifera, pteropods) or benthic animals (e.g. foraminifera, bivalves, gastropods). Each of the different habitats has a characteristic reservoir age, which increases with its water depth. If bulk carbonate is used for radiocarbon dating, a reservoir correction is hard to apply.

Table 1.1. Radiocarbon ages in radiocarbon years before present (using the Libby half life of 5568 years); no reservoir-correction; Leibniz-Labor laboratory codes are given in parentheses. Samples are core tops (0-1 cm core depth) unless otherwise indicated. Data from *Mollenhauer* [1999] (unpublished Diplom thesis).

	^{14}C age (yr BP)						
Sample	***G. sacc.***	***G. ruber***	***N. pachy. (d)***	***G. infl.***	***N. dutertrei***	***G. trunca.***	***G. crassaf.***
GeoB1711-5 (4 cm) 23.315°S, 12.377°E			[d]2030 +/-70	[e]6630 +/-60			
GeoB1721-5- 29.173°S, 13.090°E		[a]2410 +/-40			[a]2370 +/-40	[a]2550 +/-40	
GeoB1028-4- 20.099°S, 9.177°E	[c]3810 +/-70				[b]3550 +/-50		[b]3710 +/-50
GeoB1105-3- 1.665°S, 12.428°W	[a]2430 +/-50				[a]3050 +/-40		[a]3790 +/-40
GeoB1112-3-5.778°S, 10.743°W	[a]2730 +/-40				[a]3470 +/-40		[a]3000 +/-60
GeoB1505-3- 2.273°N, 33.006°W	[a]3090 +/-40				[a]4120 +/-70		[b]5220 +/-50
GeoB1515-2- 4.238°N, 43.665°W	[a]1750 +/-40				[a]1530 +/-30	[b]4590* +50 -40	
GeoB2109-3- 27.911°S, 45.870°W	1500 +/-70				970 +/-30	1580 +/-40	

Grain size fractions: [a] 250 - 355 µm
[b] 250 - 425 µm
[c] 125 - 355 µm
[d] 125-250 µm
[e] not specified

* In this sample, specimens of the two species *Globorotalia truncatulinoides* and *Globorotalia crassaformis* were analyzed together due to lack of a sufficient number of individuals of either one single species.

With the introduction of AMS, radiocarbon measurements required sample sizes were reduced to approximately 1 mg of carbon. With this opportunity it has become practicable to determine ages of monospecific samples. The advantage is that it can be assumed that all specimens have lived within the same water depth and have the same reservoir age. A reservoir age correction for near-surface dwelling planktic foraminifera of ~400 years is commonly applied. These species are commonly used in the determination of radiocarbon based age models for sediment cores. Differences between planktic and

benthic foraminiferal ages are consequently used to reconstruct ocean ventilation [e.g. *Broecker et al.*, 1990a, b].

Comparison of the ages of co-occurring planktic foraminiferal species revealed that considerable age differences may occur [*Broecker et al.*, 1988, 1999]. Bioturbation (see section 1.3.6) coupled with varying abundance histories of foraminifera can strongly influence radiocarbon ages obtained from AMS datings [*Broecker et al.*, 1999; *Mollenhauer*, 1999, unpublished]. As a result, age differences as great as several thousand years may occur between co-occurring species in one sample. Examples from a core-top study in the South Atlantic are given in Table 1.1. The results of these studies imply that for a reliable stratigraphy, abundant foraminiferal species should be used, and samples should preferably be taken at core depths of maximum species abundance.

In areas, where sediments contain little carbonate, sufficient calcite shells for radiocarbon dating may not be available. Often, total organic carbon (TOC) is used instead. Large age differences between carbonate carbon and organic carbon from identical sample intervals have been observed [e.g., *Jansen et al.*, 1984; *Summerhayes et al.*, 1995]. Total organic carbon may contain pre-aged terrestrial material and TOC radiocarbon results therefore often are biased towards older ages. The Southern Ocean, with its carbonate poor sediments is an area where radiocarbon dating of sediments is affected by these processes. Coastal upwelling systems are characterised by sediments very rich in organic carbon and poor in carbonate. At the same time, their positions close to the coast make the organic fraction susceptible to similar problems as described above for the Southern Ocean, when total organic carbon is used for radiocarbon analyses. Thus TOC ages from coastal upwelling areas are also often hard to interpret.

1.3.5 Biomarker studies

In order to obtain organic radiocarbon ages useful for marine sediment core stratigraphy, substances known to be of marine origin may be isolated. These biomarkers are ideally characteristic for a certain marine species or species group, for example alkenones as biomarkers for haptophyte algae.

The crucial aspect in biomarker dating is the compound-specific dating technique. This has been made possible by new methodologies that allow specific compounds to be isolated in high purity [*Eglinton et al.*, 1996, 1997] and by development of dedicated methods for preparation and analysis of small carbon samples by AMS [*Pearson et al.*, 1998].

Table 1.2. ^{14}C concentration in sediments from Santa Monica and Santa Barbara Basins and in corresponding DIC of surface waters [from *Pearson et al.*, 2000].

	$\Delta^{14}C$ [‰]		
Depth [cm]	DIC	TOC	Sterols
0-1	71	-62	70±3, *n=15*
4.5-5.5	-82	-149	-75±9, *n=5*

The applicability of compound specific radiocarbon for the determination of marine surface water ages where TOC ages are not reliable has been demonstrated in the Santa Monica and Santa Barbara Basins. A comparison of the $\Delta^{14}C$ of surface water DIC with the $\Delta^{14}C$ of individual phyotplanktic sterols from sediments from these basins showed that the values were very similar [*Pearson et al.*, 2000]. The results are summarized in Table 1.2. The information on the ambient radiocarbon concentration stored in biomarkers has since been used to trace the origin of n-alkanes in surface sediments [*Pearson and Eglinton*, 2000] and to prove microbial assimilation of ancient organic matter [*Petsch et al.*, 2001]. The technique holds potential to reveal pathways and timescales of organic carbon cycling.

Based on these findings, compound specific biomarker dating can now be used to generate stratigraphic information for sediment cores, where dating of calcareous fossils is not feasible. Furthermore, detailed investigations of the temporal relationship between different sediment constituents may help in understanding observed offsets and leads or lags between proxy records based e.g. on different size fraction from identical samples. Offsets between foraminiferal based records and reconstructions based on alkenones in the past have been observed and interpreted in a paleoclimatic context, even though precise age control has not been available [e.g. *Herbert et al.*, 2001].

1.3.6 Bioturbation in marine sediments

Several physical processes acting on sediment particles have the potential to influence the deposition of sediment grains and their relative position in the sediment column. One well known process is bioturbation. Reworking of older material into younger sediments and vice versa is a process that has long been recognized and investigated [e.g. *Glass*, 1969]. Deposit-feeding life has been identified to be responsible for post-depositional displacement of particles in sediments. One of the first attempts to quantitatively describe benthic mixing was made by *Berger and Heath* [1968]. Their conceptual model assumes a homogenous mixed layer of thickness X at the top of the sediment. Incoming sediment is assumed to be immediately mixed into this layer, and it is postulated that no mixing occurs below this mixed layer. The vertical dispersion patterns of microtectites in marine

sediments are in agreement with such a simple box model [*Glass*, 1969]. Later studies confirmed the findings that the simple model adequately describes most bioturbation processes, and it has subsequently been modelled in analogy with Fickian diffusion [*Guinasso and Schink*, 1975].

Bioturbation has important consequences for the interpretation of sediment core data, e.g. stable oxygen isotope records. Special caution must be taken when investigating foraminiferal $\delta^{18}O$ records from different species with variable abundance, which may result in stratigraphic offsets between two isotope records [*Hutson*, 1980]. The same process has been identified to be responsible for radiocarbon age differences between coexisting foraminiferal species [*Broecker et al.*, 1999; *Mollenhauer*, 1999 unpublished]. Events of short duration, resulting in an impulse of tracer deposited on the sediment surface (i.e. volcanic eruption, but also climatic events of short duration), may not be preserved in the sediment,

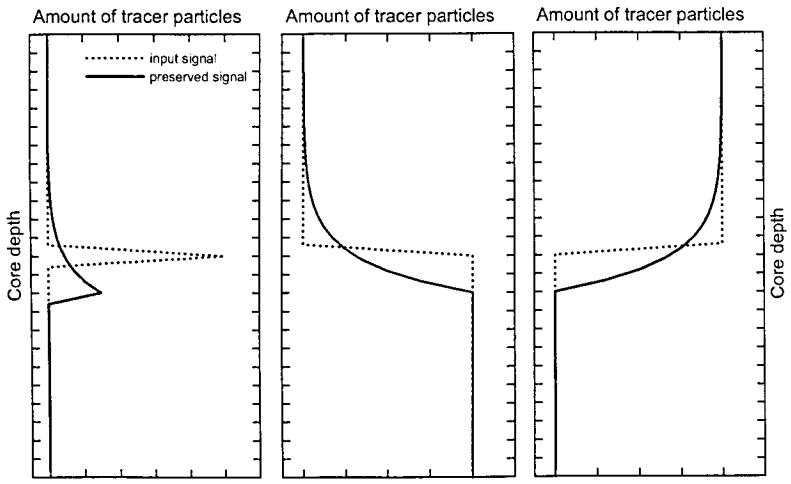

Figure 1.3. The effect of bioturbation on tracer abundance in sediments. Impulse-like signals are attenuated and displaced downward, abrupt changes are preserved as gradual increases or decreases (modified after *Berger and Heath* [1968]).

but will instead be attenuated, and the peak of tracer abundance will be displaced downward from its original occurrence [*Berger and Heath*, 1968; *Glass*, 1969; *Guinasso and Schink*, 1975; *Anderson*, 2001] (Figure 1.3).

Bioturbation results in an age-depth relationship in a sediment core which is modified from the original, ideal relationship of increasing age with increasing depth. Bioturbated sediment will have homogenous ages within the upper mixed layer, and increasing ages below the mixed layer. However, sediments in a bioturbated sediment core will be younger below the mixed layer than what would be expected in an undisturbed core without bioturbation (Figure 1.4).

Intensive research on the subject of bioturbation has shown that it is tremendously complex. Deposit-feeding may be temperature-, particle-shape- and particle-size-dependent [*Wheatcroft*, 1992], which in turn is dependent on the organisms involved. The extent to which particle size affects deep-sea sediment mixing rates is investigated experimentally and theoretically. In shallow water experiments with glass beads or metal labelled sediment, preferential mixing of fine grained particles has been proved [*Wheatcroft*, 1992; *Wheatcroft et al.*, 1994; *Shull and Yasuda*, 2001]. Efforts are currently undertaken to link bioturbation models with realistic biological reworking mechanisms [*Shull*, 2001]. The crucial aspect for deep-sea sediments, however, is that little is known about benthic fauna and characteristic feeding mechanisms at greater depths in the ocean.

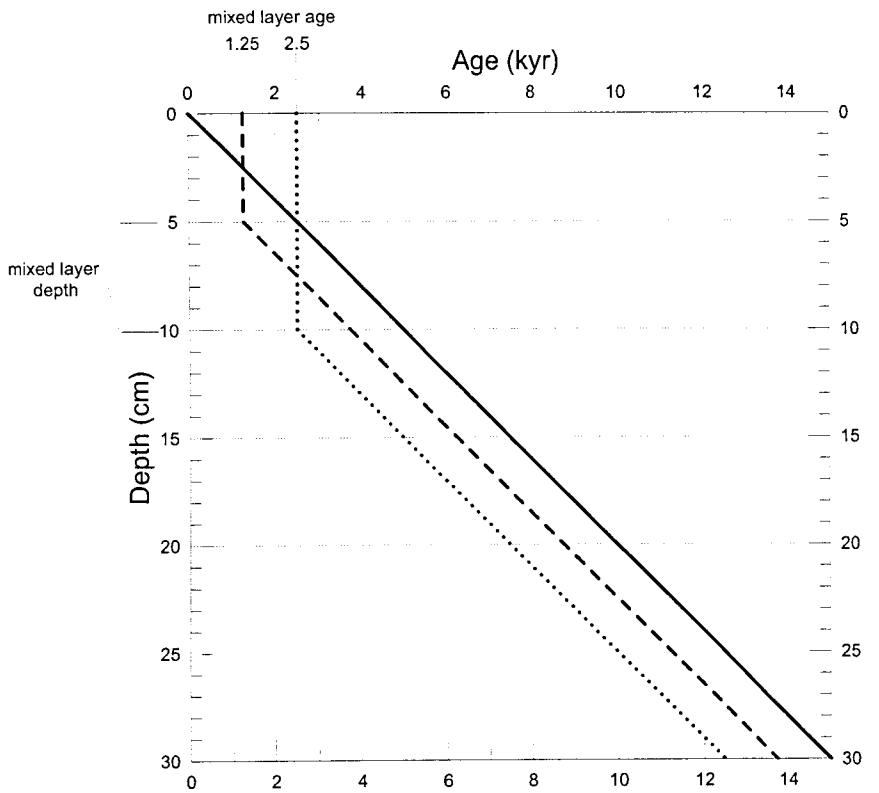

Figure 1.4. Theoretical age-depth relationships in sediment cores. The solid line represents the undisturbed, ideal age profile. The dashed line is a theoretical age-depth profile with a homogenously mixed layer of 5 cm thickness; the dotted line is the result of homogenous mixing to 10 cm core depth.

From the paleoceanographic viewpoint it is of greater importance to investigate the effect that particle selective mixing has on e.g. the relative ages of particles with different grain sizes. In theory, particles of the grain size that are mixed deeper into the sediment should be younger at a certain core depth below the mixed sediment layer than those that are mixed less deeply into the sediment (Figure 1.4). Fine grained particles should therefore be younger than coarse grained particles from the same core depth. Comparison of radiocarbon ages of foraminifera and those of fine-fraction carbonate and bulk carbonate

implies that these processes are indeed active [*Paull et al.*, 1991; *Thomson et al.*, 1995]. Further investigations showed, however, that younger fine fraction ages cannot be reproduced at all sites, and the underlying processes are far more complex [*Brown et al.*, 2000].

Bard [2001] investigated the magnitude of relative damping and phasing effects of an input signal to the sedimentary record caused by differences between bioturbation rates of coarse and fine fractions using a modification of a previous model [*Bard et al*,.1987], based on the simple box model approach. The results indicated that phase shifts and relative signal attenuation are dependent on the ratio between the mixed layer depths for fine and coarse particles. Maximum relative phase shift and attenuation are expected to be about 1 kyr and about 50%, respectively, but can be minimized by working in cores with sedimentation rates of 10-20 cm/kyr. The effect of size fraction decoupling is probably smaller than the effect of variable fluxes of proxy carriers linked with bioturbation.

A number of sophisticated mathematical and computer models have been developed in order to deconvolve bioturbated paleoceanographic proxy records [*Bard*, 1987; *Trauth*, 1998a, b; *Shull*, 2001]. However, these models can only be applied if the thickness of homogenous mixing is well known. Several techniques are applied to reconstruct mixed layer depths. High resolution radiocarbon dating of the uppermost core sections is used for estimating the mixed layer depth [e.g. *Trauth et al.*, 1997]. This radiocarbon derived mixed layer depth has been related to carbon flux to the sea-floor [*Trauth et al.*, 1997]. Comparison of mixed layer depths determined by other radionuclide tracer methods (e.g., $^{210}Pb_{excess}$) shows that often the different estimates differ significantly, which may also be a function of the time required for complete mixing [*Thomson et al.*, 2000].

Benthic deposit-feeding animals displace sediment particles in many different ways. Different bioturbation modes have been identified [see *Wheatcroft et al.*, 1994 for a review]. Reverse conveyor belt transport is a non-local movement of sediment from the sediment surface to some depth in the bed. It represents deposit feeding, tube building, or passive gravitational filling of open burrows and results in sub-surface peaks of short lived tracer data [e.g. *Wheatcroft*, 1992; *Wheatcroft et al.*, 1994; *Thomson et al.*, 2000, *Shull and Yasuda*, 2001]. The fact that these peaks are often observed implies that it may be a common mode in shallow water and deep-sea sediments. Head-down deposit feeding or excavation is a transport process of particles from some depth within the sediment to the sediment surface. It has often been observed in the laboratory but is hard to identify in the field on the basis of radiotracer data. A third possible feeding type is at the sediment surface by

organisms that do not burrow in the sediments, but it will have no effect on the vertical distribution of sediment particles.

These different transport modes may be associated with particle-size or compositional biases. These biases, however, will be dependent on the species community, and a preferential downward transport may occur either for fine or for coarse grained particles. Tests in the field [*Wheatcroft*, 1992], however, imply that fine grained particle ingestion on the sediment surface and defecation at some depth within the sediment is the dominating mechanism in many deep-sea settings.

All of the above described aspects of bioturbation make it difficult to quantify sediment reworking. With the detailed study of relative radiocarbon ages of different sediment constituents presented as Chapter 4, a contribution is made to the understanding of the importance of these processes in deep-sea sediments.

1.4 Materials and Methods

1.4.1 Samples

In this thesis, a compilation of samples collected during several cruises of R/Vs Meteor, Sonne, and Victor Hensen and from various literature sources was used. Data from the literature are referenced in the respective manuscripts (Chapters 2-4).

Surface sediment samples were obtained using a giant box corer (GKG) or a multicorer (MUC). The sediment cores were retrieved using a gravity corer (SL). Core locations are also presented in the respective manuscripts. After recovery, samples from gravity cores and box cores were taken using plastic syringes (10 ml) and stored at 4°C. Samples for organic radiocarbon analysis were takes as slices of the whole core and stored frozen at -18°C prior to processing. Multicore subcores were sectioned into 1 cm slices and stored frozen at -18°C.

1.4.2 Methods

1.4.2.1 Stratigraphy

The stratigraphy of most sediment cores is based on foraminiferal $\delta^{18}O$. A list of $\delta^{18}O$ dated sediment cores retrieved during the Special Research Project 261 (SFB261, Der Südatlantik im Spätquartär) can be found at http://www.pangaea.de/Projects/GeoB/Cores/LGM.html. Additional data were taken from the literature (Chapter 2), or generated within this thesis project. Core to core correlation of neighbouring cores on transects across the continental slope was performed for the detailed spatial investigation of the Benguela upwelling system (Chapter 3). High

resolution radiocarbon dating was carried out for some sediment cores studied in Chapter 3 and for the sediment cores investigated in Chapter 4.

1.4.2.2 Bulk sediment analyses

For bulk sediment analyses, standard methods were applied and are only briefly described here. Bulk sediments were freeze dried and homogenized using an agate mortar. From the weight loss during freeze-drying of a known sediment volume, sediment porosity, dry bulk density and water content were calculated assuming average sea-water density of 1.035 g/cm^3.

After homogenization, samples were analyzed for total carbon and organic carbon contents following the methods described by *Müller et al.* [1994]. 25 mg of sample material was weighed into tin boats and combusted under continuous oxygen flow at 1050°C in a Heraeus CHN-O-Rapid elemental analyser to determine total carbon (TC) content. For the measurement of organic carbon (TOC) content, 25 mg of the same sample was weighed into a silver boat and treated with 6M hydrochloric acid to remove carbonates. The carbonate-free sample was subsequently combusted in the same way. Carbonate was calculated from the difference between total and organic carbon and expressed as calcite ($CaCO_3$ = (TC-TOC) x 8.33).

1.4.2.3 Alkenone analysis

The unsaturation index of C_{37} alkenones ($U^{K'}_{37}$) used for the reconstruction of paleo-sea-surface temperatures was determined following standard methods. Lipids were extracted from 0.5-2 g aliquots of freeze-dried sediments using ultrasonic disrupter probes and successively less polar mixtures of methanol and methylene chloride. Extracts were desalted with de-ionised water, dried with pre-heated sodium sulphate, and purified by elution through a commercial silica gel cartridge. Clean extracts were saponified using potassium hydroxide. Finally, extracts were concentrated under a stream of nitrogen and gas chromatography was performed using a HP5890A gas chromatograph. Estimates of sea-surface temperatures were made using the equation by *Prahl et al.*, [1988]. Details of the method can be found in various publications from the Fachbereich Geowissenschaften, Universität Bremen [e.g. *Müller et al.*, 1998; *Kirst et al.*, 1999; *Rühlemann et al.*, 1999; *Benthien and Müller*, 2000; *Kim et al.*, 2002].

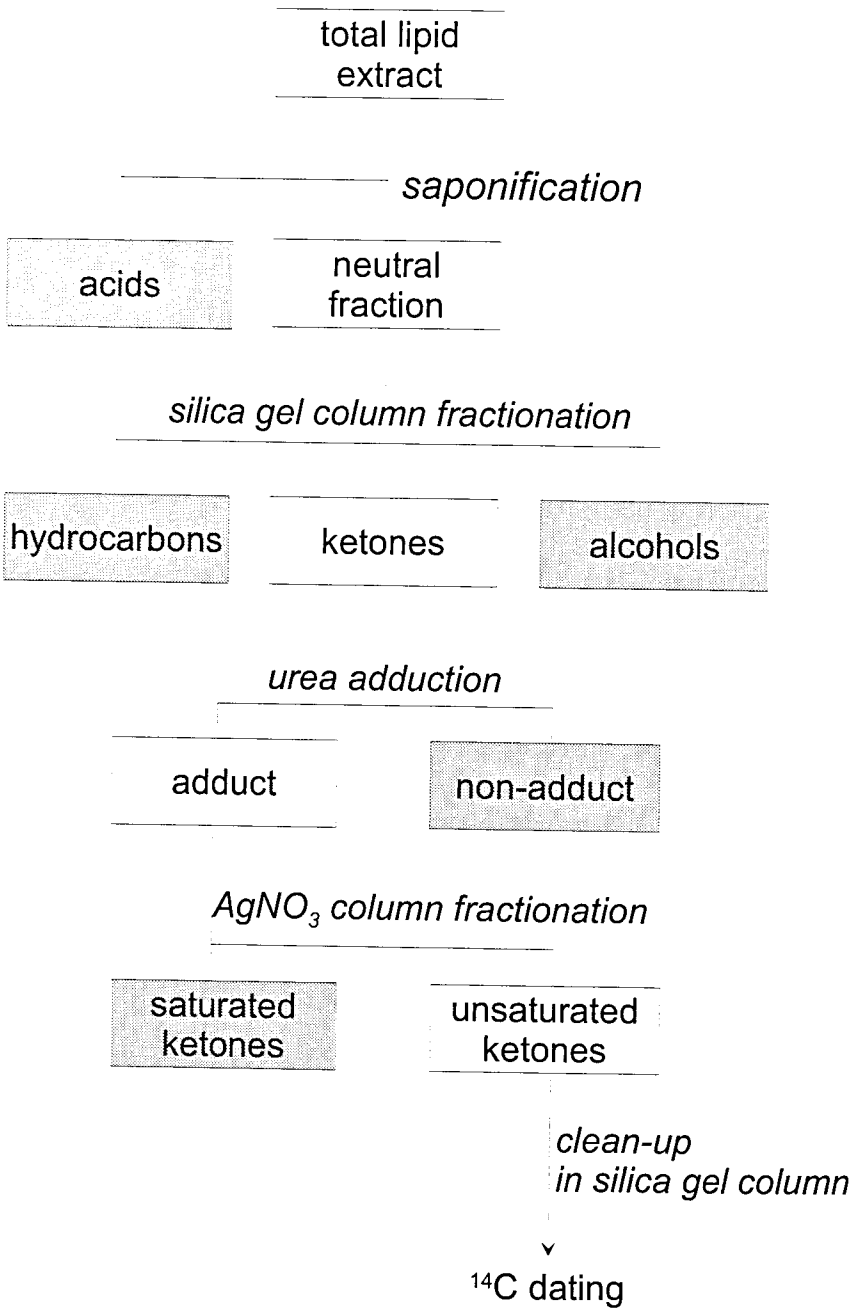

Figure 1.5. Schematic flow chart of the succession of laboratory steps for alkenone purification; fractions in shaded boxes are stored but not further processed.

1.4.2.4 Biomarker purification for radiocarbon analysis

In order to perform radiocarbon analyses of individual organic compounds, preferably source specific biomolecules (biomarkers), sophisticated techniques for quantitative extraction in high purity are required. Preparative capillary gas chromatography (PCGC) as described by *Eglinton et al.*, [1996] and by *Pearson* [2000] is a useful technique, but problems with trapping and with column bleeding arise when dealing with high boiling point compounds such as alkenones. Therefore, in this study PCGC was only used for the quantitative isolation of fatty acid methyl esters (see Chapter 4).

A new method for the isolation of C_{36}-C_{39} alkenones in high purity and in quantities sufficient for radiocarbon analysis was applied [*Xu et al.*, 2001; *Ohkouchi et al.* in prep.]. A schematic flow chart of the procedure of successive wet chemical methods is displayed in Figure 1.5. In the following paragraphs, the laboratory protocol is described in detail. All solvents used are of highest purity, and all glass ware except Soxhlet apparatuses were pre-combusted at 450°C for 8 hours.

Soxhlet extraction and saponification

Approximately 100 g of freeze-dried and homogenized sediment was weighed into a pre-solvent-cleaned (24 hours) glass ferrule with a Watman glass fibre filter covering the frit bottom. A 500mL pre-solvent-cleaned Soxhlet apparatus and ~2 litres of solvent mixture (93:7 methylene chloride (CH_2Cl_2):methanol (CH_3OH)) were used and the sediment was extracted for 48 hours. The resulting extract was rotary evaporated and transferred into a 50 mL glass vial equipped with a Teflon sealed cap. The remaining solvent was completely eliminated under a stream of nitrogen.

Approximately 15 mL of 0.5M potassium hydroxide (KOH) in methanol was added and the mixture was boiled for 2 hours at 80°C. After elimination of ~90% of the methanol under a stream of nitrogen and addition of 15 mL of distilled water, 15 mL of n-hexane was added, the mixture was shaken and the n-hexane dissolved products were transferred into a separate 50 mL glass vial. N-hexane extraction was repeated at least twice, and the combined extracts were dried under a stream of nitrogen.

Silica gel column chromatography

Silica gel (200-400 mesh; 60Å) was combusted at 450°C for 8 hours. Distilled water (1%wt.) was added for deactivation and the silica gel was shaken for 3 days. The deactivated silica gel was stored in n-hexane.

Columns were prepared in small pre-combusted Pasteur pipettes. A small quartz wool plug was inserted into the pipettes and rinsed with methanol, methylene chloride (DCM), and n-hexane. Silica gel suspended in n-hexane was filled into the Pasteur pipettes to a height of approximately 4 cm.

After re-dissolution in n-hexane, the compounds were separated into three fractions by silica gel column chromatography. To avoid column overloading, three individual silica gel columns were used for each sample, and the respective split fractions were re-combined after the separation. The first fraction containing the non-polar compounds (i.e. alkanes) was eluted with 4 mL n-hexane per column. The second fraction including alkenones was

eluted with 4 mL of a DCM:n-hexane (2:1) mixture. The more polar compounds (e.g. alcohols) were finally recovered from the columns with 4 mL methanol.

Urea adduction

The second fraction containing ketones including the alkenones was further purified by urea adduction. This method is applied for separation of straight chain molecules, such as hydrocarbons, ketones and fatty acids, with carbon numbers >14 from branched and cyclic molecules via the formation of urea clathrates. A solution of urea in methanol (40 mg/mL) is needed.

The samples were transferred into 50 mL vials and dissolved in 4.5 mL of n-hexane:DCM (2:1). While constantly shaking the mixture, 1.5 mL of urea solution were added dropwise. Consequently, the samples were refrigerated at 5°C for 15 minutes. Solvents were eliminated under a stream of nitrogen. 4.5 mL of n-hexane:DCM (2:1) were added to the crystals and the vial was vortexed for 30 seconds. The procedure was repeated at least twice. After finally eliminating the solvents, the crystals were washed with n-hexane several times, and the n-hexane fraction was pipetted into an extra vial. The urea adducted fractions containing the alkenones were recovered by dissolving the urea crystals in 15 mL distilled water and extracting the lipids with n-hexane. N-hexane extraction was repeated several times in order to maximise recovery.

Silver nitrate column chromatography

In order to separate unsaturated ketones, i.e. the alkenones, from saturated ketone molecules, silver nitrate column chromatography was applied. Silver nitrate coated silica gel was prepared by adding 20%wt. silver nitrate dissolved in excess methanol to pre-combusted silica gel. The mixture was kept at 40-45°C until methanol was evaporated. Special care must be taken to avoid exposure of silver nitrate to light, because it is photo-reactive, decays to elemental silver and looses the potential for separation of compounds. After evaporation of methanol, the silver nitrate coated silica gel was dried at 100°C overnight and stored in n-hexane in a dark glass bottle.

Columns were filled with silver nitrate coated silica gel, and the separation characteristics of the silver nitrate silica gel were tested using alkenone and saturated ketone standards and successively more polar mixtures of n-hexane and ether (5-15% ether in n-hexane) and of DCM and methanol. For the specific silver nitrate silica gel batch used for the purification of the samples prepared for this thesis, a succession of 20 mL of 5% ether

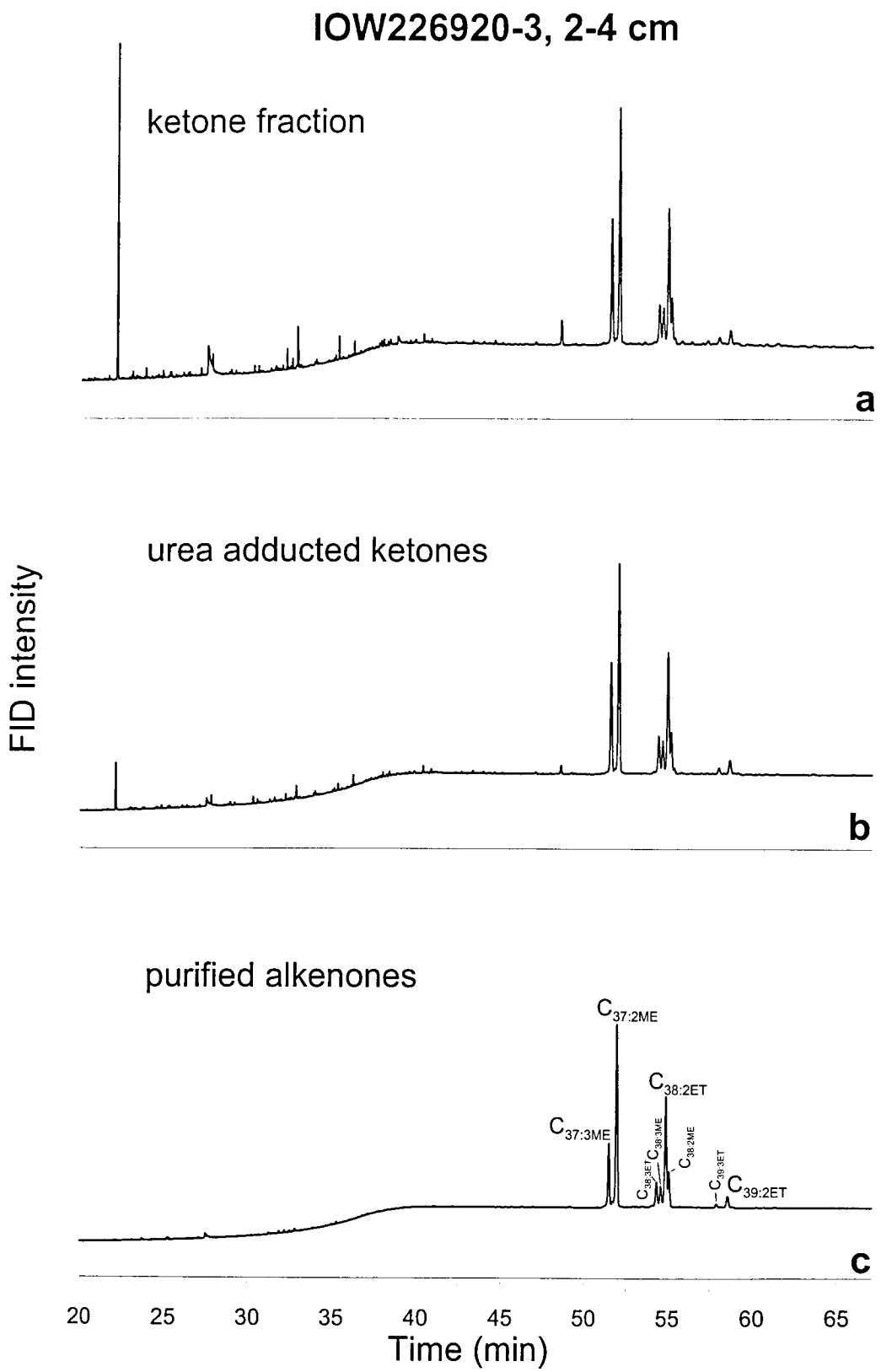

Figure 1.6. Purification of alkenones from 2-4 cm depth of core IOW226920-3. Partial chromatograms show flame ionization detector (FID) intensities. Panel (a) is a chromatogram of the ketone containing fraction after silica gel chromatography. Panel (b) shows the same sample after urea adduction. On panel (c), a chromatogram of the purified alkenone sample is displayed, and the individual compounds are identified by carbon chain length:number of double bonds; ME and ET refer to methyl and ethyl alkenones, respectively.

in n-hexane and 20 mL of 10% methanol in DCM yielded best results and highest recovery of alkenones.

A final cleaning step using silica gel column chromatography was applied after silver nitrate column separation in order to remove remaining impurities. After each of the purification steps, the progress was checked by analysing a small aliquot of the samples by gas chromatography. Examples of gas chromatograms of a sample purified by the successive cleaning steps are shown in Figure 1.6. After the final column chromatography, the amount of alkenones recovered was estimated via calibration with an external standard (behenic acid mirystyl ester).

Sample combustion

After purification, samples were transferred into pre-combusted quartz tubes (800°C, 8 hours). Solvents were evaporated under nitrogen, and approximately 2 mg of pre-combusted copper oxide, as a source of oxygen, were added. The quartz tubes were evacuated and flame sealed using a vacuum line. To prevent compounds from sublimating during the evacuation, quartz tubes were cooled with a slush of dry ice in iso-propanol (~-90°C). After flame sealing, the quartz tubes were combusted at 900°C for 8 hours. Water resulting from the combustion was stripped off the gas in a vacuum line equipped with two traps. In the first trap cooled with a slush of dry ice in iso-propanol, water was collected. In the second trap cooled by liquid nitrogen, CO_2 was separated from gases trapped at -90°C. The purified CO_2 gas was measured manometrically by expansion into a known volume, and subsequently sealed into a Duran glass tube. Comparison of gas volume and expected amount of carbon from gas chromatographic quantification was used to trace possible contamination. In most cases, gas yield from combustion compared favourably with carbon amounts estimated from gas chromatography (Figure 1.7).

The sample combustion procedure is the same for all purified compounds. For example, fatty acid methyl esters, which were collected by PCGC, were recovered from the traps and transferred into quartz glass tubes. Further processing was as described above for alkenones.

After purification, the CO_2 gas was converted to graphite. For the small, molecular level samples, Co/H_2 (Cobalt/Hydrogen) catalytic reduction is used. Details of the procedure are given in *Pearson et al.* [1998].

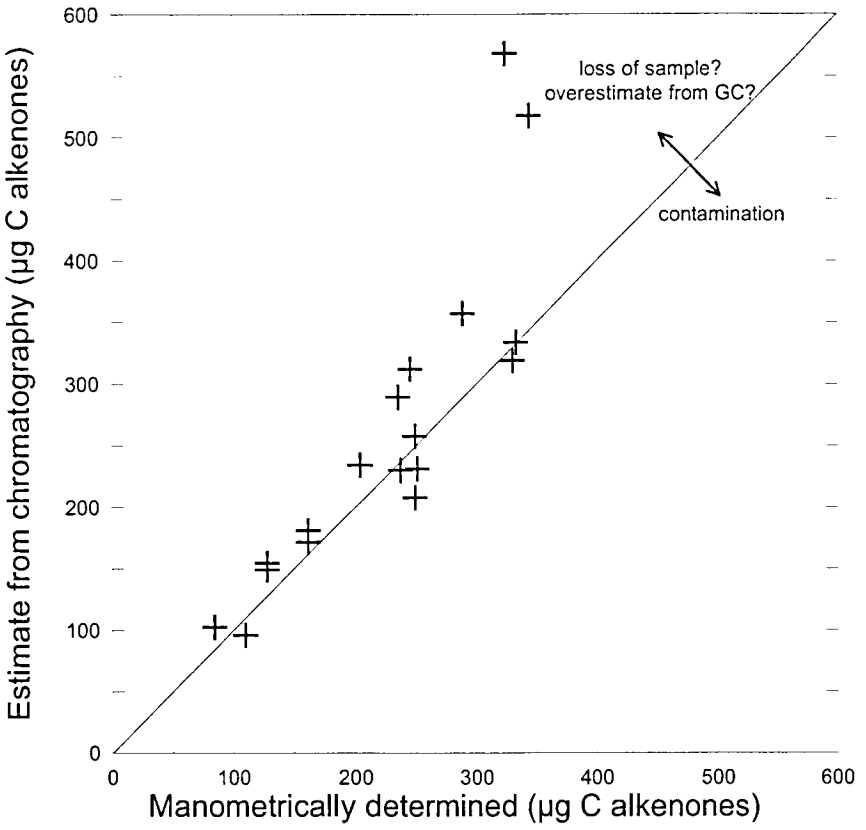

Figure 1.7. CO_2 yield after combustion vs. expected amount of compound specific carbon. The ideal relationship is indicated by the 1:1 line. Samples that plot below the line may contain carbon from contaminating sources; carbon amounts in samples plotting above the line may have been over-estimated from chromatograms or may indicate loss of sample material.

1.4.2.5 Carbonate sample preparation for radiocarbon analysis

Preparation of carbonate samples for radiocarbon analysis processing involves 3 steps: 1) cleaning to remove contamination by organic matter and atmospheric CO_2 adsorbed on the carbonate particles [*Schleicher et al.*, 1998], 2) hydrolysis and subsequent gas purification in a vacuum line, and 3) Fe/H_2 catalytic reduction.

In order to clean the carbonate particles, 10 mg sample material was weighed into reaction tubes and covered with glass beads. The reaction tubes are designed so that they can be attached to a vacuum line. 0.5mL of 30% hydrogen peroxide (H_2O_2) was added, and the reaction tubes were placed into an ultrasonic bath for 15 minutes. Supernatant peroxide was removed carefully using a Pasteur pipette, and the reaction tubes were attached to a vacuum line. Samples were vacuum dried over night. Prior to detaching the reaction tubes, the vacuum line was flushed with nitrogen in order to avoid contact of the cleaned carbonate samples with atmospheric CO_2. Hydrolysis, gas purification and catalytic reduction to graphite were performed using standard procedures [*Nadeau et al.*, 1997].

1.4.3 Mapping of geological data

Isoline maps are commonly used to represent the spatial distribution of geological data. If large data sets are processed and if quantification of a parameter is desired, computerized methods are feasible. Deriving contour maps of geological data with a computer requires the generation of a grid. A grid is a regular, rectangular array of values. Gridding produces such a regularly spaced, rectangular array of Z values from irregularly spaced XYZ data. The advantage of generating regularly spaced arrays of Z values is that, given that limits and spacing of gridded XY values are identical, grids of different Z values can be combined to create maps of dependent values. For example, grids of sedimentation rates and of dry bulk densities of sediments can be multiplied and result in a grid of mass accumulation rate if they have the same geographical range and if grid node values are spaced identically, e.g., at full degrees latitude and longitude (Figure 1.8). This method is useful for the calculation of mass accumulation rates of certain sediment constituents (e.g. organic carbon) in areas where each of the necessary input variables (sedimentation rate, dry bulk density and organic carbon concentration) is available in a different spatial resolution to the others.

An algorithm that generates grids needs to combine a method of selecting the set of control points which are used in estimating a new grid point value, and a method of calculating the estimate from the data values at that set of control points. Several different gridding algorithms are available. The method that best suits the individual data set must be chosen with care, because each has its own drawbacks [c.f. *Swan and Sandilands*, 1995].

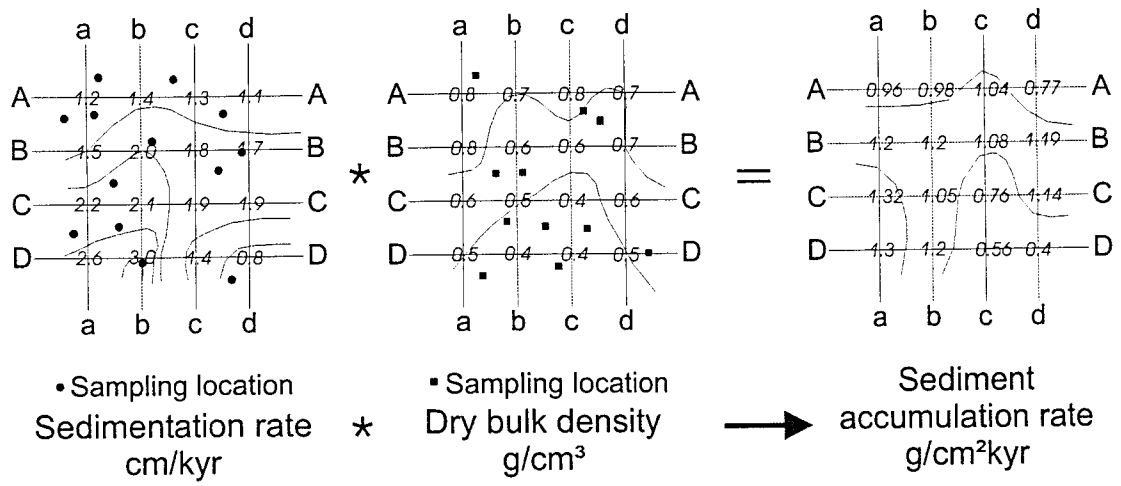

Figure 1.8. Cartoon illustrating the multiplication of grids, each based on a different set of data but with identical grid nodes.

Natural phenomena are created by physical processes. Often these physical processes have preferred orientations. For example, at the mouth of a river the coarse material settles

out fastest, while the finer material takes longer to settle. Thus, the closer one is to the shoreline the coarser the sediments while the further from the shoreline the finer the sediments. When interpolating at a point, an observation 100 meters away but in a direction parallel to the shoreline is more likely to be similar to the value at the interpolation point than is an equidistant observation in a direction perpendicular to the shoreline. Anisotropy takes these trends in the data into account during the gridding process.

The gridding method used in this thesis is "kriging", which is one of the most flexible gridding methods. Kriging is recommended for many geological purposes, because it generates a good map for most data sets. It is also a useful method, when only few data points are available. This is discussed in Chapter 3 for the Benguela upwelling region. It is based on a statistical analysis of the relatedness of control points which are specified distances apart. The result of this analysis is a variogram. The underlying principle is that on average, two observations closer together are more similar than two observations further apart. During the process of kriging, a variogram model is fitted to the data. Because the underlying processes of the data often have preferred orientations, e.g. currents for marine sediments, values may change more quickly in one direction than another. Thus, the variogram can be a function of direction. However, omnidirectional kriging is also a possible option.

The variogram is a three dimensional function. There are two independent variables (the direction θ, the separation distance h) and one dependent variable (the variogram value $\gamma(\theta,h)$) (Figure 1.9).

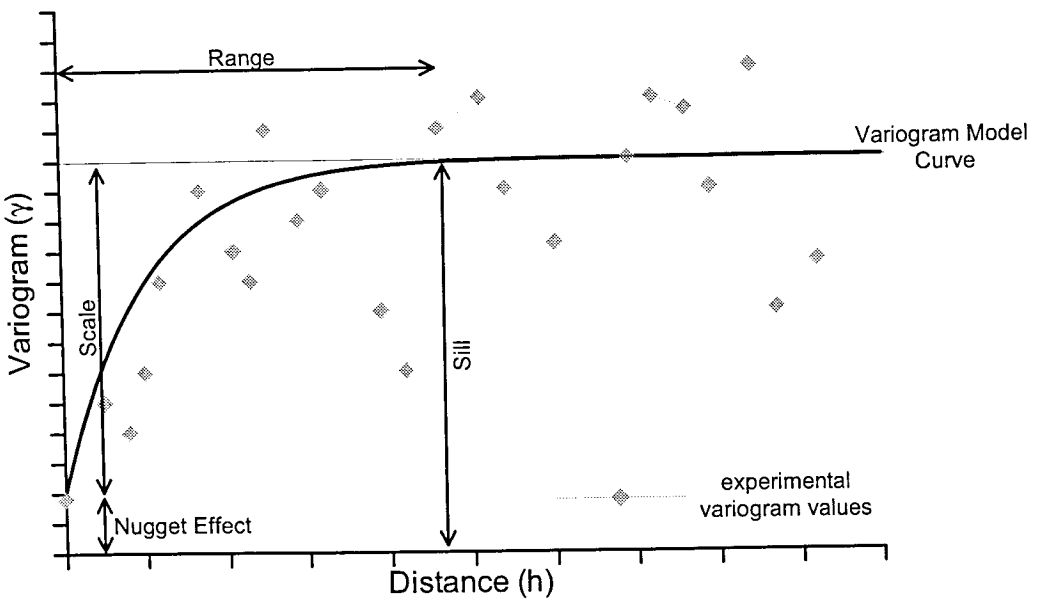

Figure 1.9. A variogram model demonstrating the variogram parameters.

The variogram model mathematically specifies the spatial variability of the data set and the resulting grid file. The interpolation weights, which are applied to data points during the grid node calculations, are direct functions of the variogram model. Variogram models can be of exponential, Gaussian, quadratic, power, spherical or logarithmic shape. A linear variogram model is a special case of a power model where the power is one. For the gridding performed in this thesis, linear kriging was used. In a linear model, the weight of data points at a specific distance from a point for which a grid node value is to be calculated is inversely proportional to its distance without further decreases in weighting with increasing distance. A linear model does not have a sill or a range. Instead, a search radius can be defined.

The maximum distance to which a data value is considered as a control point may be restricted by setting search radii. The two radii are perpendicular to each other, defining either a circular search area (if radius 1=radius 2) or a search ellipse. If a search ellipse is defined, it is advisable to arrange its orientation in the grid equal to the direction of anisotropy. In this thesis, the search radii were defined such that they allowed generating maps of the study areas without extensive gaps, but were as small as possible. The danger of choosing large search areas associated with linear kriging is that data values far away that are unrelated to the position for which a grid node value is calculated influence the calculation. This may result in smoothing of trend surfaces, and the grid may fail to reproduce extreme data values, which only occur in small sub-areas of the study area (see Chapter 2).

One possible source of errors in gridding of geologic data needs to be pointed out: If geographic co-ordinates, i.e. degrees latitude and longitude, are chosen as XY values of the data set, it has to be taken into account that a search area with two equal radii will not be circular except at the equator. The higher the latitude, the more elliptical the true search area will be with the short radius in East-West direction. Grids covering large areas have particularly large differences in search area size. Nonetheless geographic co-ordinates were used in this thesis. The reasoning is that sampling density is very variable, so that interpolations will inevitably be of unequal reliability. A possible bias that could evolve would be in a North-South direction. This is also the dominating direction of the morphologic features of the South Atlantic (i.e. the coastlines and the mid-Atlantic Ridge) that could potentially cause anisotropy. East-West trending boundaries occur only in those areas, where sampling site density is highest and distortion is smallest (e.g. the Eastern equatorial Atlantic). Possibly evolving biases would therefore support existing anisotropies rather than introducing artificial ones.

However, the lateral distortion caused by the use of geographic co-ordinates has to be taken into account for the calculation of budgets. For the calculation of budgets, e.g. of organic carbon accumulation, the gridded z values were multiplied by the area of the respective grid cell. If for instance z values represent organic carbon accumulation rates expressed as g C m^{-2} yr^{-1}, multiplication by the area (m^2) will yield the amount accumulating per year (g C yr^{-1}). The grid cells were approximated as squares with a side length equivalent to the grid node spacing at the equator. At other sites, grid cells were approximated as rectangles. With increasing distance to the equator, the East-West side lengths of these will become progressively shorter. The area of the grid cells were calculated as that of a rectangle with East-West side lengths according to the grid node's latitude. The distance (d) between two meridians (great circles perpendicular to the equator and passing through the Earth's poles) at a given latitude can be calculated as:

$$d = r_{earth} * \cos(°lat/360*2*\pi)/360*\Delta(°long) \quad (8)$$

where r_{earth} is the Earth's circumference at the equator and °lat and °long are the latitude and longitude in degrees, respectively. Δ(°long) refers to the difference between the longitudes of the two meridians, i.e. the longitudinal grid node spacing. The North-South side lengths of the rectangles are taken to be the fraction of the Earth's circumference equivalent to the latitudinal grid node spacing. This is only an approximation of the true area of the grid cells, and budgets of any parameter calculated using this procedure have to be considered estimates.

1.5 Overview of own research

The goal of this thesis is to contribute to the estimates of the role of organic carbon burial in marine sediments in the global carbon cycle, the magnitude of sources and sinks in the oceanic carbon cycle, and to contribute to the understanding of the sedimentation processes influencing organic carbon burial. The results are presented and discussed in three manuscripts.

The first manuscript aims to provide a map and a budget of organic carbon accumulation in the tropical and subtropical South Atlantic Ocean. A compilation of organic carbon concentration data and of sedimentation rates is made. Based on these data, modern annual organic carbon accumulation in the study area is estimated at $1.8 * 10^6$ t C for the pelagic region, and amounts to at least $1 * 10^6$ t C for the shelves and slopes. The latter value is most probably an underestimate, resulting from smoothing during gridding.

The importance of the shelf and slope areas as sites of organic carbon deposition is evident. The general distribution pattern resembles the pattern of modern productivity. However, productivity is not the only factor controlling organic carbon accumulation. Export efficiency and degradation of organic matter related to bottom water processes may have a significant influence, which is especially evident from the sediments in the Eastern Equatorial Atlantic. Glacial accumulation of organic matter cannot be estimated on an ocean-wide scale based on the available data. Only general trends can be depicted, which indicate that, on average, pelagic organic carbon burial increased by a factor of 2 to 3.

In the second manuscript, a detailed regional study of organic carbon accumulation is presented. Shelf and slope areas are the primary repositories of organic matter in the marine realm, and high productivity areas stand out. The Benguela upwelling area is particularly densely sampled, which allows such a detailed investigation. Lateral heterogeneity in the Benguela upwelling region requires considering information from as many sediment cores as possible. With respect to glacial/interglacial differences in organic carbon accumulation the question is addressed whether the increase of organic carbon accumulation observed in the glacial sections of many sediment cores from continental slopes underlying upwelling systems [e.g., *Sarnthein et al.*, 1988] is the result of increased productivity alone or also due to the migration of upwelling centres related to sea-level changes. In this area, locations of high productivity cells and intensity of productivity are strong factors controlling organic carbon accumulation. However, the influence of bottom currents on the deposition patterns is evident.

The third manuscript addresses the timescales on which these transport processes are active. In two sediment cores, radiocarbon dating was performed at very high resolution using foraminifera and specific organic compounds known to be of marine origin. The large age offset between the two sediment constituents suggests that they are affected by different sedimentary processes. Bottom current induced re-suspension of the fine fraction of the sediment seems to be an important process causing apparent time lags of the different records.

1.6 References

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Organic carbon accumulation in the South Atlantic Ocean: Its modern, mid-Holocene and Last Glacial basin-wide distribution

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2.1 Abstract

A compilation of 1118 surface sediment samples from the South Atlantic was used to map modern sea-floor distribution of organic carbon content in this ocean basin. Using new data on Holocene sedimentation rates, we estimated the annual organic carbon accumulation in the pelagic realm (>3000 m water depth) to be approximately 1.8 * 10^{12} g C yr^{-1}. A conservative estimate suggests that at least 1 * 10^{12} g C yr^{-1} accumulates on the shelves and slopes. Highest organic carbon contents and accumulation rates occur on the shelves, especially along the African continental margin. In the sediments underlying the divergence zone in the Eastern Equatorial Atlantic, only small amounts of organic carbon accumulate in spite of the high surface water productivity observed in that area. This is in contrast to what is found for the similar environment in the Pacific equatorial divergence, where sediments are enriched in organic carbon with respect to the adjacent pelagic areas. It implies that in the Eastern Equatorial Atlantic, organic carbon accumulation is strongly reduced by efficient degradation of organic matter prior to its burial.

During the Last Glacial Maximum (LGM), accumulation of organic carbon was higher than during the mid-Holocene along the continental margins of Africa and South America (Brazil) as well as in the equatorial region. In the Eastern Equatorial Atlantic in particular, large relative differences between LGM and mid-Holocene accumulation rates are found. This is probably to a great extent due to better preservation of organic matter related to changes in bottom water circulation and not just a result of strongly enhanced export productivity during the glacial period. On average, a 2 to 3 fold increase in organic carbon accumulation during the LGM compared to mid-Holocene conditions can be deduced from our cores. However, for the deep-sea sediments this cannot be solely attributed to a glacial productivity increase, as changes in South Atlantic deep-water circulation seem to result in better organic carbon preservation during the LGM.

2.2 Introduction

The transfer of carbon through the marine reservoirs plays a key role in controlling atmospheric CO_2 concentrations. Carbon burial in marine sediments is a major process affecting the amount of carbon stored in the ocean-atmosphere system [*Berner*, 1982, *Reimers et al.*, 1992]. However, only a very small proportion of surface water primary production reaches the deep sea, owing to intense remineralization in the euphotic zone, during settling of particles and at the sea-floor. Nevertheless, the accumulation of organic carbon (C_{org}) in deep-sea sediments over longer time-scales removes significant amounts of carbon from the ocean-atmosphere system. In addition, calcium carbonate dissolution in sediments and thus the sea water's carbonate chemistry is linked to the supply and oxidation of organic matter. Increased dissolution of calcium carbonate will add alkalinity and dissolved inorganic carbon (DIC) to the ocean, which in turn will cause atmospheric CO_2 levels to decrease. Increases in C_{org} to calcite rain ratios will lead to atmospheric CO_2 drawdown [e.g. *Archer and Maier-Reimer*, 1994; *Sigman et al.*, 1998; *Sigman and Boyle*, 2000].

Calculations of annual primary productivity by now are rather well constrained [*Antoine et al.*, 1996; *Behrenfeld and Falkowski*, 1997]. Export of this organic matter to the deep ocean varies significantly in different regions [*Antia et al.*, 2001]. It is highest along continental margins, particularly in upwelling areas [e.g. *Berner*, 1982; *Fischer et al.*, 2000]. At tropical and subtropical open ocean sites, export fluxes are low to moderate, while in the polar regions of the Atlantic, export of organic matter is very low [*Lampitt and Antia*, 1997; *Fischer et al.*, 2000], as is the proportion buried in the sediments [e.g. *Berger et al.*, 1994]. As was pointed out by *François et al.* [1997], the Southern Ocean's influence on atmospheric CO_2 concentration is controlled by water stratification rather than by C_{org} burial, as the depth of the winter mixed layer determines the effectivity of organic carbon remineralization. A shallow depth of the winter mixed layer in the low latitude ocean, in contrast, makes the tropics more effective in carbon export and sequestration [*Antia et al*, 2001]. While a lot of data exist on export of organic matter below the euphotic zone, surprisingly little is known about the spatial variability in the fraction of primary production that ultimately reaches the sea floor and is buried in the sediments. Only crude estimates exist for the amount of annual C_{org} accumulation in mid to low latitudes. An investigation of carbon burial in tropical and subtropical areas may thus provide important information on the role of C_{org} burial in the global carbon cycle.

Terrestrial organic matter transported by rivers and dust also significantly contributes to the burial of C_{org} in low to mid-latitude sediments [e.g. *Schlünz and Schneider*, 2000]. The major portion of suspended particles is discharged by rivers in the tropical and subtropical regions

[*Milliman and Meade*, 1983]. As a result of this spatial distribution of terrestrial input and of marine productivity and its export as described above, it has been estimated that the majority of C_{org} flux to the deep sea occurs within 30° of latitude north and south of the equator [*Jahnke*, 1996].

In the above context, the tropical and subtropical South Atlantic can be considered as an oceanic region that is characterized by relatively high overall productivity [*Berger and Wefer*, 1996] and by major rivers draining South America and Africa. In past studies of organic carbon distribution and accumulation [e.g. *Curienk*, 1986; *Berner*, 1982; *Jahnke*, 1996] this region, however, was underrepresented in terms of data. We therefore compiled published and own data on sedimentary C_{org} content in core tops and on Holocene sedimentation rates from the tropical and subtropical South Atlantic, and generated maps of both parameters. Based on these maps, modern C_{org} accumulation rates were calculated in order to investigate its spatial distribution and to estimate in-situ annual burial rates of C_{org}. The data on spatial distribution were compared with theoretical estimates of organic carbon burial derived from maps of primary productivity [*Antoine et al.*, 1996] using an export flux equation [*Suess*, 1980] and considering the effect of differences in bulk sedimentation rates [*Berger et al.*, 1989].

Increased strength and efficiency of the biologic pump has been proposed to be one of the mechanisms responsible for the lower atmospheric CO_2 concentrations during the last glacial [e.g. *Broecker and Peng*, 1986; *Sarnthein et al.*, 1988]. However, studies of glacial export productivity have indicated that glacial-interglacial changes, if present at all, are relatively small. For instance, glacial export productivity has been shown to be approximately equal to modern export productivity in the Atlantic Sector of the Southern Ocean [*Frank et al.*, 2000]. Similar levels of glacial and Holocene C_{org} accumulation are reported from the polar North Atlantic [*Taylor et al.*, 2002]. Estimates from the Benguela upwelling system imply that Holocene and LGM C_{org} accumulation rates are approximately equal [*Mollenhauer et al.*, in press; Chapter 3]. While most of these studies have focused on areas characterised by enhanced productivity at present, a comparison of glacial and Holocene C_{org} accumulation in the pelagic regions of the Atlantic Ocean is still lacking, and sediment drift bodies and sediment input by ice rafting in the mid latitude North Atlantic complicate such an investigation. We therefore compared mid-Holocene (4-8 kyr BP) and LGM (19-23 kyr BP) rates of C_{org} accumulation in the tropical and subtropical pelagic South Atlantic. Mid-Holocene accumulation rates are preferred over modern values in order to avoid biasing the younger rates towards higher values in latest Holocene rates due to non-equilibrium diagenetic conditions characterised by still active C_{org} degradation in the near-surface sediments.

Increased glacial accumulation of C_{org} has been reported for core sites from a wide range of environmental settings in the tropical and subtropical Atlantic Ocean [e.g. *Curienk*, 1986; *Sarnthein et al.*, 1988; *Summerhayes et al.*, 1995; *Bertrand et al.*, 1996]. However, at some sites, glacial accumulation was lower than during the Holocene, or glacial-interglacial differences are negligibly small [e.g. *Diester-Haass*, 1985; *Curry and Lohmann*, 1990; *Schmidt*, 1992; *Bertrand et al.*, 1996]. Uncertainty is also enhanced because reliable Holocene and Last Glacial C_{org} accumulation data are only available from a limited number of sediment cores. Based on a number of new sediment cores we compare Holocene and glacial C_{org} accumulation rates from various oceanographic settings in the South Atlantic in order to depict general trends in glacial-interglacial differences.

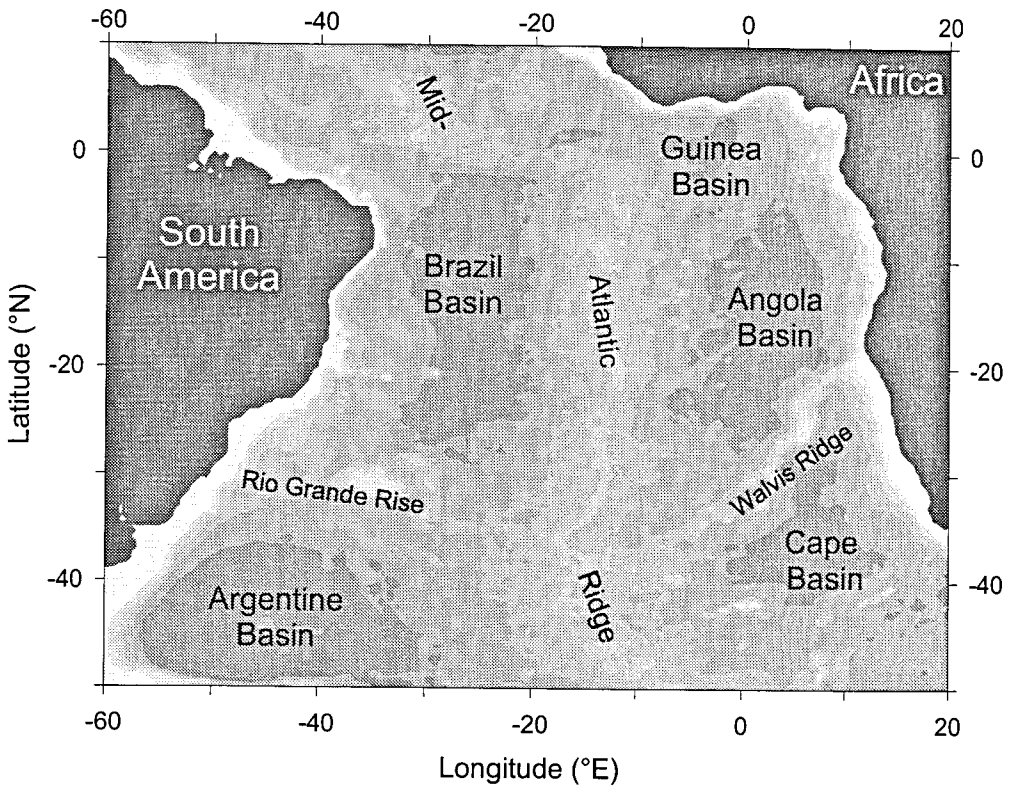

Figure 2.1. Map of the study area in the South Atlantic. Major deep sea basins and bottom topographic features referred to in the text are indicated.

2.3 Study area

This study focuses on the tropical and subtropical South Atlantic between 10°N and 40-50° S and between 60° W and 20° E. The South Atlantic is subdivided into five major deep sea basins. The Brazil Basin north of the Rio Grande Rise and the Argentina Basin south of it are located west of the Mid Atlantic Ridge. The two basins are connected by a narrow deep

incision called the Vema Channel. The eastern basins are, from North to South, the Guinea Basin, the Angola Basin and the Cape Basin. The latter two are separated by the Walvis Ridge (Figure 2.1).

The surface water circulation patterns are dominated by the subtropical gyre, which is composed of the Benguela Current in the East, the South Equatorial Current in the North, the Brazil Current in the West and the northernmost branches of the Antarctic circumpolar current in the South. Detailed reviews on the circulation pattern can be found in e.g. *Peterson and Stramma* [1991] and *Reid* [1996].

The deep water circulation in the tropical and subtropical South Atlantic involves two major bodies of water, both with characteristic salinity and concentrations of oxygen and CO_2. These are the Antarctic Bottom Water (AABW) and the North Atlantic Deep Water (NADW). For a detailed description the reader is referred to *Reid* [1989]. The bottom water in the western basins is composed of cold AABW relatively rich in nutrients and poor in oxygen. The NADW in contrast is rich in oxygen but poor in nutrients and flows at depth along the eastern boundary of the South Atlantic, moving southward. South of 45-50°S the NADW mixes with the Circumpolar Deep Water and leaves the Atlantic Ocean in an eastward direction.

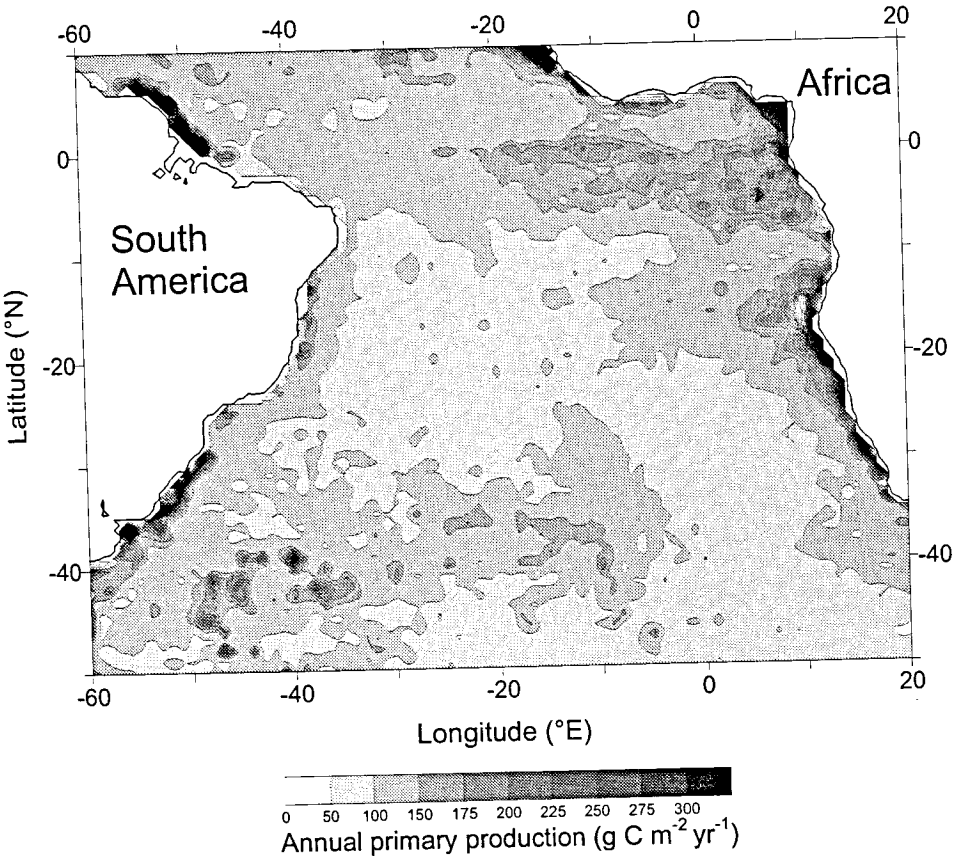

Figure 2.2. South Atlantic annual primary production according to *Antoine et al.* [1996]. The data were computed based on the upper ocean chlorophyll-like pigment concentration as measured by CZCS satellite images.

The modern distribution of primary productivity (PP) in the South Atlantic is asymmetric, with the higher rates occurring in the eastern basins (Figure 2.2). At present, a high PP area fuelled by high nutrient input from coastal upwelling processes is observed off Southwest Africa [*Shannon*, 1985; *Shannon and Nelson*, 1996]. Further north, PP is fostered by nutrients discharged from the Congo and Niger rivers, which in turn are dependent on the amount of monsoonal precipitation and chemical weathering in the hinterland [*van Bennekom and Berger*, 1984; *Schneider et al.*, 1997]. In the Eastern Equatorial Atlantic (EEA), enhanced PP resulting from open ocean upwelling is observed. The subtropical gyre is a large oligotrophic region. PP is also low in the Western Equatorial Atlantic. Off the coast of southern South America, high pigment concentrations in surface waters indicate enhanced PP due to oceanic upwelling or surface water mixing at oceanic fronts.

2.4 Materials and Methods

2.4.1 Modern organic carbon distribution

For comparison of sedimentary organic carbon distribution with the modern patterns of organic carbon production in the South Atlantic surface waters, we used annual primary productivity data as determined from satellite imagery by *Antoine et al.* [1996]. These data are available in a 1° x 1° grid resolution from ocean colour remote sensing. The computation of productivity as described by *Antoine and Morel* [1996] is based on the monthly global maps of the photosynthetic pigments that were derived from the "Coastal Zone Color Scanner" (CZCS) data archive The method yields values for computed global annual primary production (PP) that range between 36.5 and 45.6 Gt C $yr^{-1}$and a value for annual PP in the study area of approximately 4.6 Gt C yr^{-1} [*Antoine et al.*, 1996].

For the sedimentary synthesis, we compiled surface sediment C_{org} data from the literature and own data obtained over the last decade. This compilation comprises 1118 individual sites, many of which are located along the continental margins (Figure 2.3). The highest density of sampling sites is found off Namibia. The African continental margin in general is sampled more intensively than the South American continental margin. Sampling density is still low for the deeper ocean basins, with some regional gaps in the central Brazil Basin. A complete list of sampling sites shown here can be found on the data archive PANGAEA (http://www.pangaea.de). It includes data published by *Lisitzin et al.* [1975], *Emelyanov and Romankevich* [1979], *Müller and Suess* [1979], *Curry and Lohmann* [1982], *Jansen et al.* [1984], *Cwienk* [1986], *Tiedemann* [1986], *Svalnov et al.* [1988], *Levitan et al.* [1990], *Westerhausen et al.* [1993], *Mackensen et al.* [1994], *Müller et al.* [1994], *Romankevich* [1994], *Sarnthein et al.* [1994], *Hübner* [1995], *Bickert and Wefer* [1996], *Jennerjahn and Ittekkot* [1997], *Schmiedl et al.* [1997],

Jennerjahn et al. [1999], *Rühlemann et al.* [1999], *Wagner* [1999], *Haese et al.* [2001], *Mollenhauer et al.* [in press; Chapter 3], *Wagner et al.* [submitted] and *Frenz et al.* [submitted].

The C_{org} contents are expressed in weight percent of dry, salt-free sediment assuming a pore water salinity of 35 ‰ for own data, or as stated in the respective references for the data from other sources as cited above. Methods of measurement and sampling devices are as described by *Müller et al.* [1994] or in the references listed above.

2.4.2 Modern, Mid-Holocene, and Last Glacial C_{org} accumulation rates

C_{org} accumulation rates, expressed as g C m^{-2} yr^{-1}, were calculated by multiplying C_{org} content, sediment dry bulk density, and sedimentation rate. For estimation of modern C_{org} accumulation rates, core-top C_{org} contents were combined with dry bulk density values from core top sediments and Holocene sedimentation rates. The latter were calculated by linear age interpolation between the core top and the first tie point derived from oxygen stable isotope stratigraphy, radiocarbon ages, or as described in the respective references below. This type of Holocene sedimentation rates are available for 200 core sites, also listed in PANGAEA (http://www.pangaea.de). The data set includes data published by *Mix et al.* [1986], *Müller and Suess* [1979], *Imbrie et al.* [1984], *Jansen et al.* [1984], *Balsam and McCoy* [1987], *Curry and Crowley* [1987], *Curry et al.* [1988], *Broecker at al.* [1991], *Charles et al.* [1991], *Schneider* [1991], *Bickert* [1992], *Meinecke* [1992], *Thießen* [1993], *Kemle-von Mücke* [1994], *Müller et al.* [1994], *Sarnthein et al.* [1994], *Sikes and Keigwin* [1994], *Verardo and McIntyre* [1994], *Rühlemann* [1996], *Little et al.* [1997], *Müller et al.* [1997], *Gingele et al.* [1998], *Arz et al.* [1999], *Brathauer and Abelmann* [1999], *Gingele et al.* [1999], *Kirst et al.* [1999], *Rühlemann et al.* [1999], *Frank et al.* [2000], *Vogelsang et al.* [2001] and *Mollenhauer et al.* [in press; Chapter 3]. The number of sites with available Holocene sedimentation rates is again highest in the upwelling area off Namibia. The Congo fan and the Eastern Equatorial Atlantic areas are also well represented. Only very few estimates of sedimentation rates exist for the Western South Atlantic, in particular for the deep Brazil and Argentine Basins. As each of the three parameters necessary for the calculation are available for different sites and in a different regional site density, modern C_{org} accumulation rates are calculated by combining the computed grids of the three parameters (see below) instead of calculating values for individual sites.

For 77 cores sites in the South Atlantic, C_{org} accumulation rates are also available for the LGM (19-23 kyr BP, as defined by *Mix et al.* [2001]). Most of the cores were retrieved from the continental slope off West Africa, on the Walvis Ridge, near the eastern equatorial high productivity area, and on the Ceará Rise off North-East Brazil. These sites have been considered for a basin-wide comparison of Last Glacial to Holocene C_{org} accumulation rates.

In order to achieve comparability of Holocene and LGM accumulation rates, we could not use the above compilation of recent C_{org} accumulation rates. Core-top C_{org} contents, in contrast to LGM values, are in diagenetic disequilibrium due to still ongoing decomposition of organic carbon near the sediment-water interface. To avoid biasing the calculated values for the interglacial situation towards values that are too high with respect to glacial values, mid-Holocene values were calculated from sedimentation rates and organic carbon content in core sections covering the time interval between 4 and 8 kyr BP. For the calculation of the mid-Holocene and LGM accumulation rates, data published by *Jansen et al.* [1984], *Curry and Lohmann* [1990], *Bickert* [1992], *Meinecke* [1992], *Schmidt* [1992], *Sarnthein et al.* [1994], *Rühlemann* [1996], *Schneider et al.* [1996], *Gingele et al.* [1998], *Arz et al.* [1999], *Wagner* [2000] and *Mollenhauer et al.* [in press; Chapter 3] were used. A list of sites and accumulation rates is available on the data archive PANGAEA (http://www.pangaea.de).

2.4.3 Mapping

Based on the data set of organic carbon content in surface sediments, a 1° x 1° grid of C_{org} content in the South Atlantic was generated using isotropic kriging with a linear variogram model [*Davis*, 1986]. The search radius was restricted to 8° in latitude and longitude in order to avoid unreasonably long distances for interpolation.

The grids computed contain data values for each grid node at the intersection of lines of full degrees latitude and longitude. The grids for different parameters were all calculated in the same format, which allowed them to be multiplied by each other.

The relatively coarse spatial resolution of our grid does not allow resolution of discrete patterns along continental margins, which are areas of highly variable productivity and sedimentation, as well as being the areas of highest C_{org} contents. The true C_{org} content at individual sites in these areas may exceed the values given on the map [cf. *Mollenhauer et al.*, in press; Chapter 3], because for coarse grid intervals, as used here, average values are calculated over a larger area and steep gradients are not resolved. This problem has to be borne in mind when discussing the gridded patterns along continental margins, which should not be regarded as quantitative estimates.

For a basin-wide estimate of modern accumulation of organic carbon in the South Atlantic, the grids of C_{org} content, sedimentation rate and an additional one for sediment dry bulk density based on data from 361 of the surface sediment sites were multiplied. When multiplying these grids, modern annual modern organic carbon accumulation can be estimated in a 1 x 1 ° spatial resolution. We corrected for the latitudinal distortion by calculating each grid cell area as a rectangle with a width according to the respective latitude. Areas that appear

blank on the maps of C_{org} content or sedimentation rate due to insufficient data were assigned a typical pelagic value of C_{org} accumulation (0.01 – 0.02 g C m^{-2} yr^{-1}) estimated by comparison with neighbouring grid cells. Due to insufficient spatial resolution, we did not determine C_{org} accumulation rates for the southern Cape Basin and adjacent parts of the Mid Atlantic Ridge (south of 40°S).

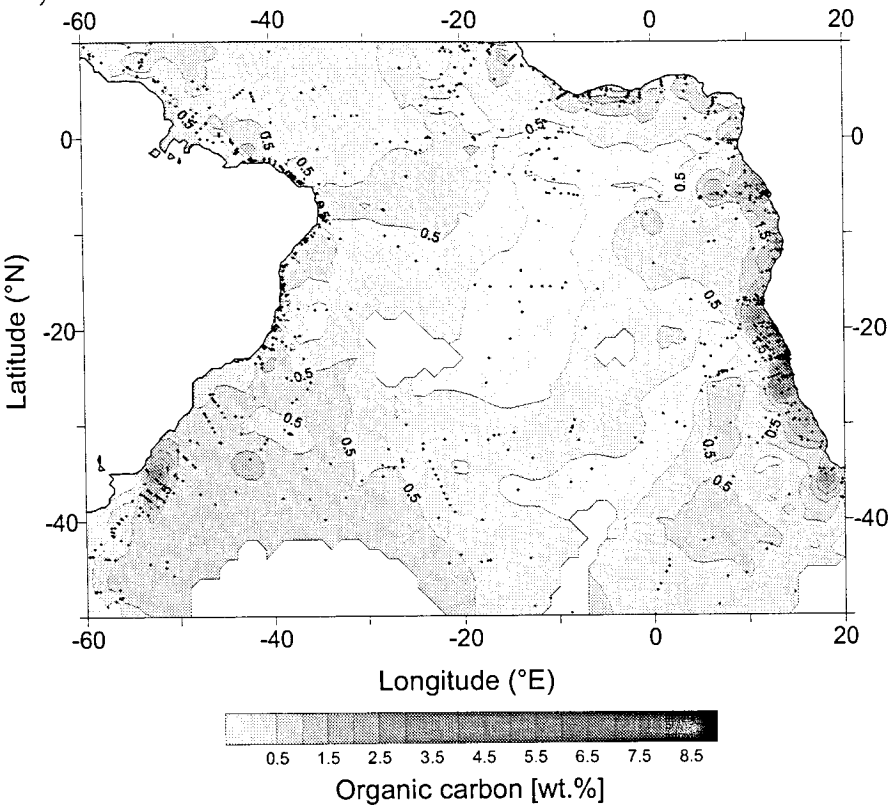

Figure 2.3. Organic carbon content in surface sediments in the South Atlantic. Sample locations are indicated by the dots. White areas are blanked during the gridding procedure (isotropic linear kriging with an 8° search radius) due to insufficient spatial resolution.

2.5 Results and Discussion

2.5.1 Organic carbon content in surface sediments

The regional distribution of organic carbon in surface sediments is shown in Figure 2.3. High C_{org} content of up to 9 % of total dry weight are observed along the continental margins. In general, the sediments from the eastern continental margin of the South Atlantic contain more C_{org} than those from the western continental margin. The highly productive Benguela upwelling system off Southwest Africa with its extremely high sedimentary C_{org} contents reaching values >20% is the most prominent of these areas.

Another region with sediments significantly enriched in C_{org} is the Congo River fan. The isotopic and elemental composition of the organic material suggests that only shelf and upper slope deposits close to the river mouth contain high proportions (>50%) of terrigenous

organic matter, while sediments in water depths greater than 700 m have predominantly marine organic material [*Müller et al.*, 1994]. The sediments near the mouth of the Amazon contain only small amounts of C_{org}, as terrestrial organic matter discharged by the river is not deposited directly offshore from its mouth. Instead it is dispersed by alongshore currents, while on the Amazon fan, modern organic carbon accumulation is dominated by authochthonous marine production [*Müller-Karger et al.*, 1988; *Schlünz et al.*, 1999; *Schlünz et al.*, 2000]. Another fluvial system that may contribute to enhanced C_{org} contents in western margin sediments is the Rio de la Plata discharging into the Argentine Basin. However, in this ocean basin a large amount of sediment is transported laterally over long distances, which is a process governed by deep-water current activity. Thus organic-rich fine-grained particles may be focused in the north-western corner of this basin [*Benthien and Müller*, 2000].

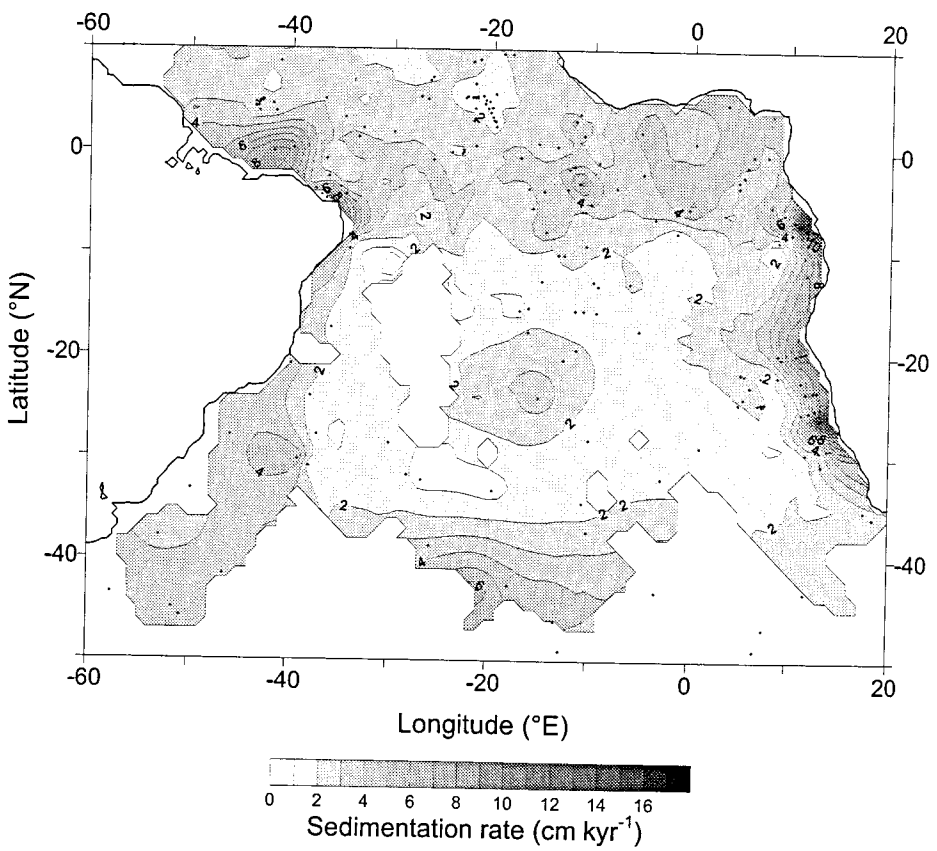

Figure 2.4. Holocene sedimentation rates in the South Atlantic. Dots indicate sampling locations of cores. White areas are blanked during the gridding procedure (isotropic linear kriging with an 8° search radius) due to insufficient spatial resolution.

Pelagic sediments generally contain only small amounts of organic carbon. Here, surface sediment contents do not exceed 1% and are generally below 0.3%. Examples of pelagic areas where surface sediments are relatively rich in C_{org} are the Argentine Basin south of the Rio Grande Rise, extending a little further north through the Vema Channel, the north-eastern corner of the Brazil Basin and the neighbouring flank of the Mid Atlantic Ridge, as well as the

deep Cape Basin. Lowest organic carbon contents are found on elevated parts of the sea floor such as the Mid Atlantic Ridge and the Walvis Ridge. This can largely be attributed to dilution of the organic carbon by carbonate accumulating in shallower water depths (compare with the carbonate map by *Archer* [1996]).

2.5.2 Holocene sedimentation rates

Figure 2.4 is a map of Holocene sedimentation rates. The distribution pattern of sedimentation rates resembles that of C_{org} content. The highest sedimentation rates of up to 10 - 15 cm kyr^{-1} occur off Southwest Africa, off the Congo River and along the north-eastern coast of South America. The pelagic part of the South Atlantic is characterized by low sedimentation rates between 1 and 2 cm kyr^{-1}. The low spatial resolution in the Argentine Basin is due to the presence of large sediment drift bodies which complicate the establishment of stratigraphic control of sediment cores.

Table 1. Compilation of published data on annual organic carbon accumulation.

Reference	Ocean area	Area (10^6 km^2)	Annual C accumulation (10^{12} g)	Avg. annual C accumulation per area (g m^{-2} yr^{-1})
Reimers et al. [1992]	slopes and rises			0.72 - 1.2
Wollast [1998]	shelves	26	200	7
	slopes	32	40	1.3
	open oceans	300	4	0.01
Berner [1982]	Indian open ocean	65	1.2	0.02
	Pacific open ocean*	135	0.8	0.006
	Equ. Pacific	11	0.8	0.07
	Atlantic open ocean	74	3.6	0.05
	SW Africa upwelling	0.03	1.5	50
Mollenhauer et al. [in press; Chapter 3]	SW African shelf	0.15	0.5-2.15	3.3-14
	SW African slope	0.24	0.32	1.3
this study	South Atlantic >3000 m	30	1.8	0.06
	< 3000 m	5	1+	0.2+

*excluding equatorial high productivity area
+minimum values

In general, sedimentation rates are susceptible to errors caused by uncertainties in age models. Also, the assumption of a linear increase in age between discrete dated sediment levels yields average constant sedimentation rates for given time intervals between these tie points, which may not be the case in reality. This can cause artefacts because calculated sedimentation rates do not represent deposition at an instant in time. Nevertheless the map in Figure 2.4 represents magnitude and distribution of sedimentation rates, as errors at individual sites are expected to become less important when generating interpolated grids.

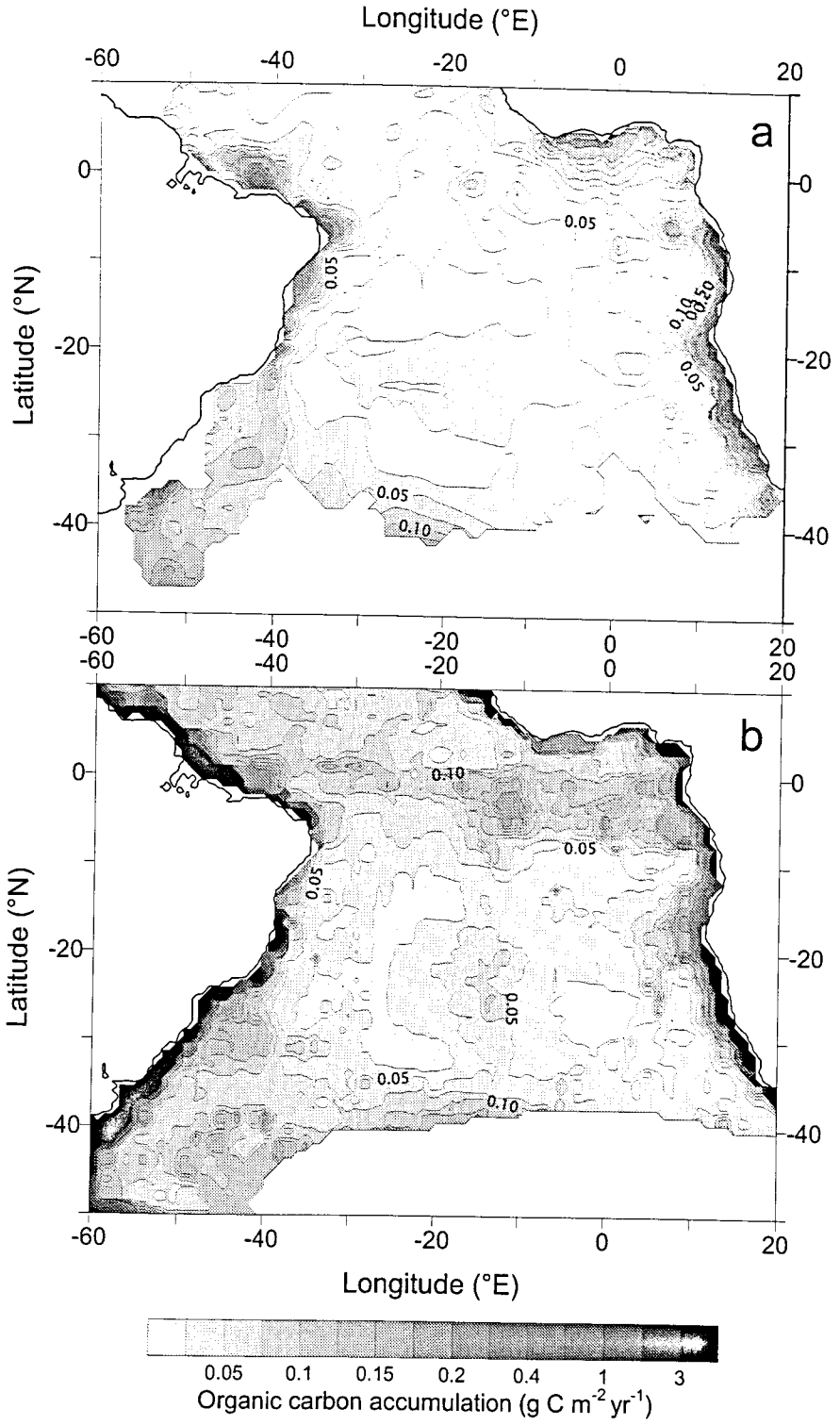

Figure 2.5. a) Organic carbon accumulation rates based on C_{org} content in surface sediments, Holocene sedimentation rates and surface sediment dry bulk density. b) Expected organic carbon accumulation calculated from surface water primary productivity data (Antoine et al., 1996) using the equation from Suess (1980) for flux (J) with J_{Corg} = PP/(0.0238z+0,212) for z<600 m and J_{Corg}= 40PP/z for water depth below 600 m (z=water depth), and equation 10 from Berger et al. (1989) for C_{org} accumulation (F_{sed}) with $F_{sed}=J_{Corg}(2.5SR-SR^2/50)$.

2.5.3 Estimate of modern annual organic carbon accumulation

Figure 2.5a depicts modern C_{org} accumulation. Very high rates are found along the continental margins, in particular along the African coast. In contrast, in the pelagic realm, accumulation rates are relatively low and show little lateral variability. Based on this distribution, basin-wide annual organic carbon accumulation was estimated. The result is compared with published data on deep-sea burial of organic carbon in different areas of the world's oceans (Table 1). When only considering pelagic areas at water depths greater than 3000 m where accumulation is relatively homogenous, and excluding high deposition areas on the continental shelf and slope, we estimate an annual C_{org} accumulation of ~$1.8 * 10^{12}$ g C yr^{-1} over an area of approximately $30 * 10^6$ km^2. This corresponds to an average accumulation of 0.06 g C m^{-2} yr^{-1} in the open ocean. Our results compare favourably with those of *Berner* [1982], who calculated annual burial of organic carbon for the entire pelagic Atlantic Ocean to be on the order of $3.6 * 10^{12}$ g C yr^{-1}, corresponding to an average of 0.05 g C m^{-2} yr^{-1}.

According to our estimate, the narrow continental margins, representing only $5 * 10^6$ km^2, account for an additional accumulation of $1.0 * 10^{12}$ g C yr^{-1}. This, however, is a conservative estimate, as the steep gradients in C_{org} accumulation occurring across the shelves and slopes cannot be resolved in a 1° x 1° grid. The high accumulation rates in coastal environments are likely to be underestimated when averaging over a larger area (i.e. the search area; see section 3.3). A higher resolution study was carried out in the densely sampled Benguela System in the South Atlantic. For this area, modern annual C_{org} accumulation was estimated to be on the order of $2.5 * 10^{12}$ g C yr^{-1}, 86 % of which occurs on the shelf [*Mollenhauer et al.*, in press; Chapter 3]. This implies that the annual burial in the Benguela system is almost equal to the total annual organic carbon accumulation in the entire pelagic South Atlantic, reinforcing the important role of the shelves already pointed out by *Berner* [1982]. Nonetheless we will focus on the pelagic area in the following discussion, because of the lack of consideration in particular of the equatorial upwelling areas given in former studies of past changes in the marine organic carbon cycle.

2.5.4 Organic carbon accumulation and estimated flux to the sea-floor

In the past, organic carbon accumulation has been used to reconstruct productivity in surface waters [e.g. *Müller and Suess*, 1979; *Sarnthein et al.*, 1992, *Taylor et al.*, 2002]. The underlying assumption is that, if terrigenous input can be neglected, the amount of C_{org} that is buried in the sediments is directly related to PP, and can be described as a function of PP, water depth and sedimentation rate. Empirical equations have been derived based on limited data sets [*Müller and Suess*, 1979; *Stein*, 1986; *Sarnthein et al.*, 1992]. With our data set it is now

possible to investigate the applicability of these assumptions on a basin-wide scale by comparing satellite derived maps of PP and basin-wide C_{org} accumulation.

Ignoring the contribution of organic carbon from terrestrial sources into the South Atlantic, which according to our unpublished carbon isotope data of bulk organic matter in the pelagic sediments outside the major river fans never exceeds 10% of the total organic carbon, we compared measured total organic carbon accumulation in surface sediments with theoretical C_{org} fluxes to the sea floor. Equations have been proposed to relate export productivity at a certain water depth to PP in the photic zone. This approach takes into account that overall fluxes decrease with increasing water depth, where organic matter is remineralised during its passage through the water column [e.g. *Suess*, 1980; *Betzer et al.*, 1984; *Antia et al.*, 2001]. For depths below a few hundred meters, the equation by *Suess* [1980] reduces to a simple relationship inversely proportional to depth. Here we applied the Suess equation to the productivity data by *Antoine et al.* [1996] to estimate flux to the sea-floor. From this flux, we estimated sedimentary C_{org} accumulation according to *Berger et al.* [1989], which we will refer to as expected C_{org} accumulation rate (Figure 2.5b).

In general, distribution patterns of high C_{org} accumulation rates along the continental margins and lower and less variable rates in the deep sea basins are clearly evident from both maps (Figure 2.5a, b). The expected accumulation rates on the shelves are generally higher than what has been observed. This is interpreted as an artefact due to the coarse gridding resolution used for calculation of the observed accumulation rates (see discussion in section 3.3 about problems with low gridding resolution). Continental shelf and slope sediments are highly heterogeneous, influenced by sedimentary processes such as current induced winnowing, and are often characterized by high sedimentation rates which promote organic matter preservation. Several additional factors such as low bottom water oxygen content and/or focusing of fine-grained material must be considered as factors also influencing C_{org} accumulation. If detailed assessments of fluxes and accumulation in these areas are desired, high resolution regional studies must be carried out, such as presented e.g. by *Bremner* [1983], *de Haas and van Weering* [1997], *de Haas et al.* [1997], *Gardner et al.*, [1997] or *Mollenhauer et al.*, [in press; Chapter 3].

There are also remarkable differences between expected and observed C_{org} accumulation in the pelagic realm, where sedimentation rates are relatively low and homogenous. One of the areas where these differences are evident is the Eastern Equatorial Atlantic (EEA). While the estimate derived from sediment data (Figure 2.5a) indicates that in the EEA C_{org} accumulation is low and does not vary significantly from deep sea areas underlying oligotrophic surface ocean conditions, the map of the expected accumulation (Figure 2.5b) shows a distinct belt of

high values underlying the high productivity area in the EEA. It is not likely that this discrepancy is an artefact due to insufficient spatial resolution of the data. In contrast, the EEA is one of the areas with good sample coverage (compare Figures 2.3 and 2.4). Therefore the difference between expected and observed C_{org} accumulation in the EEA could either be due to regionally different export efficiency of organic matter from the surface waters or to effects related to C_{org} preservation.

Regional variations in export efficiency have been deduced from sediment trap data [*Fischer et al.*, 2000; *Antia et al.*, 2001]. For the EEA moderately high values have been calculated [*Fischer et al.*, 2000]. Moreover, the EEA is an area with pulsed rather than continuous production [*Longhurst*, 1993], which increases the potential of high rates of C_{org} export and sequestration [*Berger and Wefer*, 1990; *Buesseler*, 1998; *Antia et al.*, 2001]. Therefore, other potential processes causing low C_{org} accumulation underneath the EEA divergence zone must be considered.

Various factors influencing the content of C_{org} in deep-sea sediments have been identified along with the flux of organic matter to the sea floor. One factor controlling preservation of C_{org} is the bulk sediment accumulation rate, partly determining oxygen exposure time, with enhanced preservation at high rates of sediment accumulation. This effect is accounted for in the equation for C_{org} accumulation derived from PP [*Berger et al.*, 1989]. Further factors that have been discussed are the oxygen content of bottom and pore waters, the composition of the organic matter, and the surface area of sediment grains, as organic matter is easily adsorbed on clay minerals [*Müller and Suess*, 1979; *Stein*, 1986; *Canfield*, 1994; *Mayer*, 1994; *Hedges and Keil*, 1995; *Hartnett et al.*, 1998].

For the discussion of potential mechanisms responsible for the low accumulation rate of C_{org} in the Eastern Equatorial Atlantic it is noteworthy that in the Eastern Equatorial Pacific (EEP), which is also a high productivity area related to open ocean open ocean upwelling, surface sediments contain up to 3 % of organic carbon. This is a substantial enrichment compared to neighbouring pelagic sediments from the oligotrophic Pacific [*Berner*, 1982; *Curienk*, 1986]. Furthermore, average deep export ratios in the Pacific are lower than in the Atlantic [*Lampitt and Antia*, 1997]. Thus higher rates of C_{org} accumulation would be expected in the Atlantic rather than in the Pacific. The process in question for the EEA is therefore likely to be a deep-water effect and characteristic for the specific situation in the Atlantic Ocean.

Bottom water circulation in the Atlantic Ocean is distinctly different from the Pacific. Age and corrosiveness of bottom water, i.e. its dissolved CO_2 and O_2 concentrations, influence preservation of C_{org} on the sea floor. Bottom water circulation in the eastern South

Atlantic, particularly in the Guinea Basin, is dominated by North Atlantic Deep Water, which is rich in oxygen and poor in nutrients and CO_2. Thus, conditions in the deep Guinea Basin below the EEA high production zone do not favour organic carbon preservation as they may do in the EEP. This kind of strong influence of northern component deepwater on bottom water chemistry and the resulting decrease in the preservation potential of organic matter in the eastern equatorial South Atlantic has already been proposed by *Curry and Lohmann* [1990].

2.5.5 Mid-Holocene versus LGM C_{org} accumulation rates

Mid-Holocene and LGM C_{org} accumulation rates for 77 sediment cores are compared in Figure 2.6. Due to the coarse spatial resolution, it was not feasible to estimate glacial organic carbon accumulation for the whole tropical and subtropical South Atlantic. Nevertheless, general trends of glacial-interglacial changes in organic carbon accumulation can be inferred from the data available.

Sediments below the EEA divergence zone are characterised by relatively low (0.01-0.5 g C $m^{-2}yr^{-1}$) organic carbon accumulation rates both during the Holocene and during the LGM (Figure 2.6a and b). However, the factor of glacial increase (Figure 2.6c) is high (on average 5- to 6-fold) in most of the cores from this area when compared to other cores, including those from the coastal high productivity system off South-West Africa (on average 2- to 3-fold).

In the EEA, the increase in glacial C_{org} accumulation is the result of strongly increased sedimentary C_{org} contents in the LGM sections of the cores rather than increased sedimentation rates. If enhanced PP alone were responsible for such an increase in C_{org} accumulation, bulk sedimentation rates would also be expected to increase. In the Benguela high productivity system, for example, increases in calculated C_{org} accumulation during the LGM result from increases both in C_{org} content and in sedimentation rate [*Mollenhauer et al.*, in press; Chapter 3].

Presently, the bottom water in the Guinea Basin underlying the EEA divergence is predominantly of northern origin (NADW) and rich in oxygen. These bottom water conditions are assumed to have prevailed during the entire Holocene. Glacial reduction of NADW production has been proposed in many studies [e.g. *Sarnthein et al.*, 1994]. *Curry and Lohmann* [1990] suggested that a stronger influence of CO_2-rich and oxygen-poor southern component deep-water during the last glacial period was the cause for such a Holocene-LGM difference in organic carbon preservation at water depths below 3750 m. This agrees with the model proposed by *Boyle* [1988]. The stronger influence of southern component deep water during the glacials in the tropical Atlantic was also confirmed by *Verardo and McIntyre* [1991]

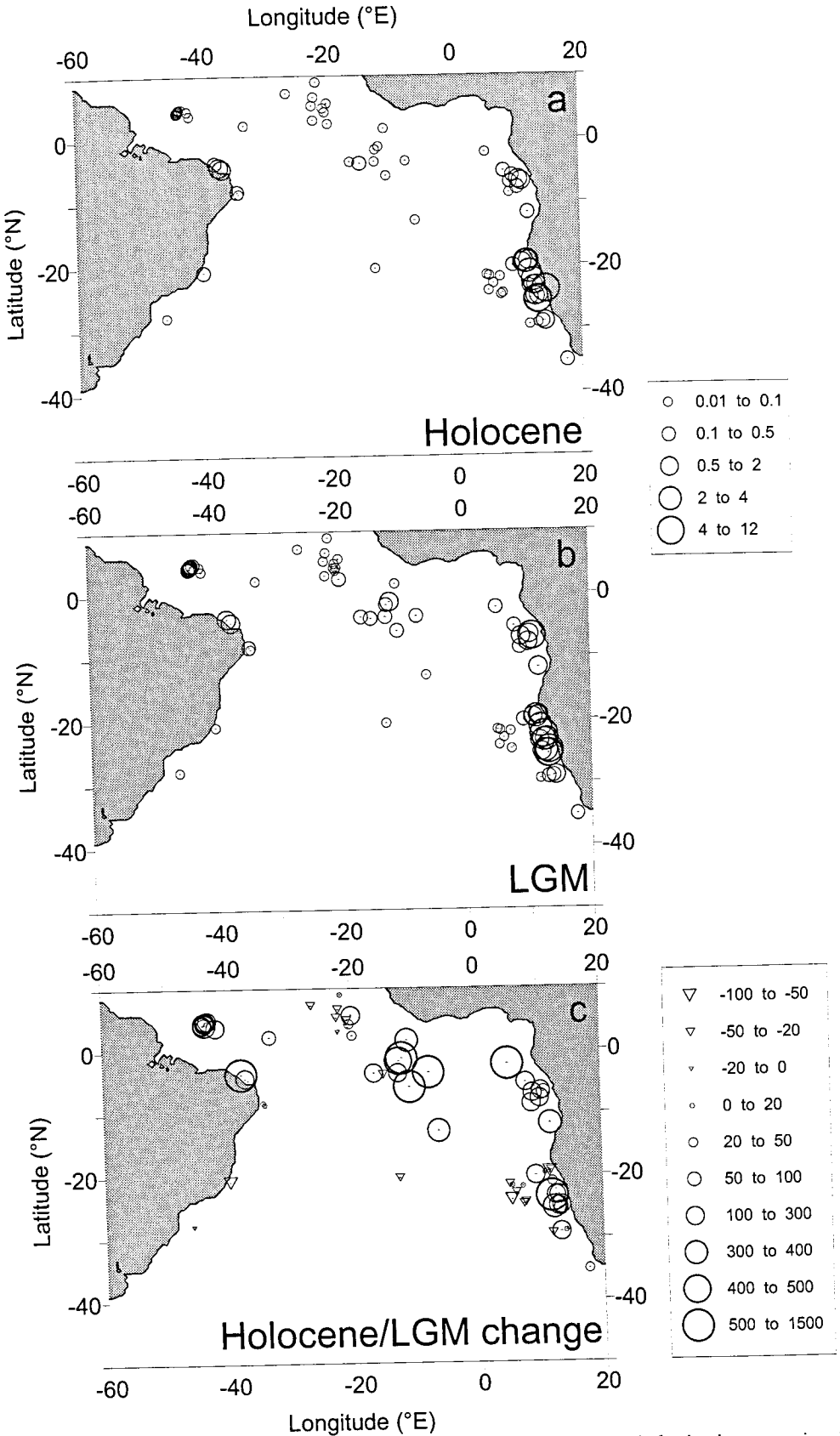

Figure 2.6: a) Mid-Holocene (4-8 kyr) C_{org} accumulation rates in units of g C m^{-2} yr^{-1}; circle size is proportional to accumulation rate (upper legend). b) C_{org} accumulation rates in units of g C m^{-2} yr^{-1} during the LGM; circle size is proportional to accumulation rate, same scale as in a). c) Ratio of LGM increase in C_{org} accumulation with respect to Holocene in percent. Negative values (triangles) are glacial decreases (lower legend).

and *Bickert and Wefer* [1996]. During the LGM, southern component deep water extended further north and was found higher in the water column than today, promoting carbonate dissolution. Decreased carbonate contents with respect to the Holocene are observed in glacial sediments of the EEA [*Catubig et al.*, 1998]. Together with lower bottom water oxygen concentrations, this decrease in carbonate content may have increased deep-water alkalinity. Both property changes in the deep ocean are favourable for enhanced C_{org} preservation in the EEA during glacial times.

On the other hand, it has been suggested in studies based on proxies independent from C_{org}-accumulation that upwelling intensity in the EEA was strongly increased during the LGM, enhancing productivity in surface waters [*Meinecke*, 1992; *Gingele and Dahmke*, 1994; *Mix and Morey*, 1996]. This should have resulted in increased rates of organic carbon accumulation in the underlying sediments. The evidence presented in these studies must be taken into account when interpreting the five- to six-fold increase in organic carbon accumulation in glacial sediments from the EEA. The strong increase in organic carbon accumulation in the EEA is therefore probably the result of the combination of mainly two effects: increased PP in surface waters and better preservation of organic matter during the LGM due to a deep-water mass change.

In more recent studies, the ratio of PP that is exported below the photic zone and has the potential to be preserved in the sediment was found to be also dependent upon food web structure [*Buesseler*, 1998], which in turn is postulated to be, among other factors, a function of surface water temperature [*Laws et al.*, 2000]. Thus a glacial change in food web structure, shifting toward a population dominated by larger diatoms that favour export of particulate organic carbon, may additionally contribute to the observed effect of increased glacial organic carbon accumulation in the EEA. Increased diatom abundance and opal content during the LGM have been reported for cores from the EEA [*Verardo and McIntyre*, 1994]. The model by *Laws et al.* [2000] also predicts a strong increase in export ratio when temperature decreases in areas of intermediate to high PP, for instance if temperature changes from 26°C to 23°C. This is the temperature difference between the Holocene and the LGM reconstructed for the EEA [*Schneider et al.*, 1995].

Along the African continental margin, high rates of C_{org} accumulation prevailed during the mid-Holocene, and values for the Last Glacial Maximum are even higher. One exception to this general picture of increased glacial C_{org} accumulation along the African continental margin is the outer Walvis Ridge. Here, organic carbon accumulation rates are low both during the Holocene and the LGM, and at some sites, the glacial C_{org} accumulation was even lower than during the Holocene (Figure 2.6c). These low glacial C_{org} accumulation rates are

related to very low sedimentary C_{org} contents (generally <0.1%) rather than to decreases in sedimentation rates. Sediment trap studies suggest high export efficiencies at the outer Walvis Ridge [*Fischer et al.*, 2000], and estimated fluxes to the sea-floor are in relatively good agreement with modern C_{org} accumulation (Figure 2.5). While faunal analyses [*Oberhänsli*, 1991] imply that productivity has been enhanced during the LGM, decreases in opal accumulation during glacials have been interpreted as decreases in productivity under cold climatic conditions [*Diester-Haass*, 1985]. In order to explain this paradox, it has been proposed that upwelling may have been increased but restricted to a narrow zone close to the coast during the glacials, while during interglacial times, the band of high productivity was wider [*Diester-Haass*, 1985; *Berger and Wefer*, 2002]. Another possible explanation for decreased C_{org} accumulation on the outer Walvis Ridge is winnowing caused by intensified bottom currents.

Low rates of organic carbon accumulation prevail in the Western Equatorial Atlantic both during the mid-Holocene and during the LGM. The area is characterized by low PP and therefore probably does not contribute significantly to total pelagic organic carbon accumulation both during the mid-Holocene and during the LGM. Two cores from the upper continental slope off North-East Brazil are exceptions. Glacial and deglacial sedimentation processes at these sites were dominated by fluvial input of terrigenous material [*Arz et al.*, 1998] and strongly increased glacial organic carbon accumulation rates are primarily caused by increased runoff rather than by higher productivity.

Overall, the LGM to mid-Holocene ratios of C_{org} accumulation from all 77 cores imply that during the LGM, accumulation of organic carbon in the tropical and subtropical South Atlantic was two to three times higher than during the Holocene. The exceptional high factor of 5 to 6 in parts of the pelagic realm, namely the Eastern Equatorial Atlantic, is not related to increases in PP alone, because deep-water chemistry in the Atlantic Ocean changed dramatically between glacial and interglacial conditions. Furthermore, it has to be taken into account that the shelves, which are the primary deposition centres for organic carbon in the modern ocean and presently account for at least as much C_{org} accumulation as the pelagic realm, were exposed during the glacials. Together with the results from the Southern ocean this implies that total accumulation may be assumed to have not been much different between glacial and interglacial periods.

2.6 Conclusions

- In most parts of the tropical and subtropical South Atlantic organic carbon accumulation in modern surface sediments is mainly controlled by productivity of the overlying surface waters. The high productivity in the Eastern Equatorial Atlantic related to upwelling, however, is not reflected by high C_{org} accumulation rates in the underlying sediments. This may mainly be due to intense degradation of the sedimentary organic material bathed in oxygen rich NADW.

- Total annual accumulation of organic carbon is on the order of $1.8 * 10^{12}$ g C in the pelagic South Atlantic (>3000 m water depth). A conservative estimate of the continental margins suggests that at least $1 * 10^{12}$ g C is annually accumulating on the shelves and slopes.

- During glacial times, increases in organic carbon accumulation are significant along the continental margins. High relative glacial increases of C_{org} accumulation occur in the EEA, which is not related to PP increases alone. Instead a combination of increased upwelling resulting in enhanced primary productivity and better preservation of the organic material in the sediments in response to changes in oxygen concentration and alkalinity of South Atlantic deep-water masses seem to be responsible. On average, glacial C_{org} accumulation rates in the pelagic South Atlantic were two to three times the Holocene accumulation rates in our cores. The role of continental shelf areas for modern C_{org} accumulation needs to be considered when attempting total budgets.

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Glacial/interglacial variability in the Benguela upwelling system: Spatial distribution and budgets of organic carbon accumulation

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3.1 Abstract

Modern sedimentary total organic carbon (TOC) content as a proxy for surface water export production was mapped on the shelf and on the upper continental slope of the Benguela upwelling system using 137 core tops. Shelf maxima in TOC can be correlated with maxima in surface water productivity. On the slope, high TOC contents are observed offshore from sites of strong modern upwelling. Estimates of modern TOC mass accumulation rates (MAR) show that approximately 85 % of the total is accumulating on the shelf.

TOC MAR were calculated, mapped and budgeted for the Holocene and for the Last Glacial Maximum (LGM) using 19 sediment cores from the continental slope. During the LGM, centres of production and deposition have migrated off-shore with respect to their Holocene positions. TOC accumulation on the continental slope was approximately 84 % higher during the LGM than during the Holocene, possibly reflecting enhanced productivity.

The TOC distribution patterns and sediment echo-sounding data suggest that undercurrents strongly influence the sedimentation off Namibia. Winnowing and focusing result in great lateral heterogeneity of sedimentation rates and sediment properties. Individual cores therefore do not necessarily reflect general changes in export production. These results highlight the need for detailed regional studies based on a large number of sediment cores for highly heterogeneous high productivity areas in order to derive general statements on total fluxes.

3.2 Introduction

Among the mechanisms proposed for glacial CO_2 drawdown as observed in ice cores [e.g. *Petit et al.*, 1999] is a glacial increase in oceanic productivity, causing greater carbon burial rates in marine sediments [e.g. *Sarnthein et al.*1988]. This increased "biological pumping" should be observable in high productivity and upwelling areas of mid and low latitudes, accounting for 80 – 90 % of the modern world's new production [*Summerhayes et al.*, 1995a]. The linkage between carbon cycling in high productivity upwelling systems and the nutrient reservoirs of the deep ocean through time, however, remains uncertain. The issue is important, because changes in the nutrient source for upwelling may have had an impact on the extent to which upwelling centres changed from being sources or sinks for carbon [*Summerhayes et al.*, 1995a]. In order to extract more CO_2 from surface waters during the glacials, low-latitude carbon export may then have been driven by e.g. an increase in the source water nutrient reservoir and/or a change in the composition of the export production [*Sigman and Boyle*, 2000]. As *Summerhayes et al.* [1995a] pointed out, chemical budgets, particularly for carbon, for all upwelling systems are of key importance for the understanding of the role of the biological pump in modulating atmospheric CO_2 levels. It is still unclear whether coastal upwelling is responsible for a large or a small part of the carbon sequestered in marine sedimentary reservoirs [*Summerhayes et al.*, 1995a].

With respect to glacial/interglacial export productivity changes in coastal upwelling systems, two major effects have been discussed: An intensification of upwelling due to stronger trade winds and a lateral displacement of the centres of high productivity as a result of sea-level lowstand. Both would lead to higher TOC accumulation in glacial sediments at a given site on the continental slope. Glacial/interglacial variations in TOC accumulation in coastal upwelling systems may however also be influenced by changes in the amount of terrigenous input. The shelf as a site of major modern TOC accumulation and as a depositional environment which is significantly influenced by glacial sea-level lowstands must also be taken into consideration.

Evidence for higher glacial productivity has been reported from detailed studies of total organic carbon (TOC) content in various cores from the two high productivity areas off Northwest and Southwest Africa [*Sarnthein et al.*, 1988, *Summerhayes et al.*, 1995b, *Abrantes*, 2000]. However, lower productivity for glacials has also been postulated based on individual sites from these coastal upwelling systems [*Diester-Haass*, 1986; *Martinez et al.*, 1999]. *Gardner et al.* [1997] observed decreased glacial productivity at some sites off Western North America. *Bertrand et al.* [1996] presented a study based on two piston cores from the Northwest African

coastal upwelling system showing that both increases and decreases in glacial productivity can be observed at different sites within a few degrees of latitude in one high productivity system. Due to such regional heterogeneity, general statements on productivity histories based on few core sites prove to be difficult.

As a consequence of the considerations above, it is advisable to attempt a regional budget based on as many core sites as possible in order to understand the general glacial/interglacial variability in a certain high productivity system. We present a case study for the Benguela system off Namibia. The area has been extensively sampled and a large number of geochemical and sedimentological analyses have been carried out on surface sediments and down-core material [*Schneider et al.*, 1995, *Müller et al.*, 1997, *Little et al.*, 1997a, b, *Kirst et al.*, 1999, *Lavik*, 2001, *Jahn et al.*, subm.]. Terrigenous input of organic matter is expected to be insignificant at all times due to the aridity of the area. The role of the shelf is also particularly interesting off Namibia, as the Southwest African continental margin has a deep and wide shelf, much of which remained flooded even at times of lowest sea-level during the Last Glacial Maximum (LGM). Therefore, the area appears to be suitable for a more detailed investigation and may provide new important information on the quantitative nature of past variations in "biological pumping".

3.3 Study area

The major part of the Benguela high productivity system is located off Southwest Africa adjacent to the coasts of Namibia and South Africa (Figure 3.1). Its northern and southern boundaries are defined as the Angola-Benguela frontal zone and the Agulhas retroflection, respectively. The Walvis Ridge forms the northern boundary of the Cape Basin and at about 19.5°S is connected with the continental shelf via a shallow (> 2500 m) sill, which we will refer to as Walvis Plateau. The shelf width and depth in the Cape Basin are variable. Double shelf breaks are common, in particular near Walvis Bay (23°S). The outer shelf is relatively deep in large areas with the major shelf break at a water depth of about 400 m.

The wind field in the Benguela area is dominated by the trade wind system, as described in detail by *Shannon and Nelson* [1996]. Upwelling favourable winds are perennial in the northern part of the system, while in the South, distinct upwelling maxima occur in spring and summer. Consequently, the upwelling system is commonly divided into a northern part with perennial upwelling and a southern half with stronger seasonality. The border between the two

subsystems is usually drawn near Lüderitz at 27°S. In this study, we focus on the northern subsystem.

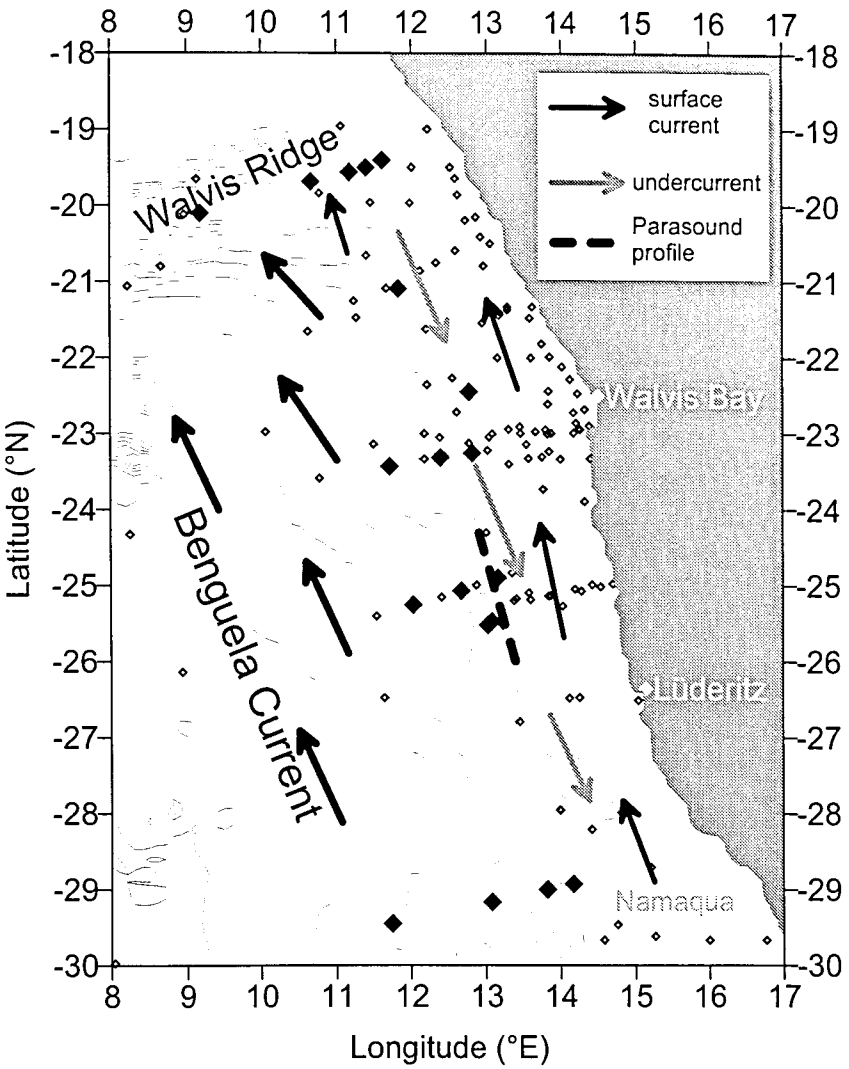

Figure 3.1. Study area and core sites (core tops: open symbols, sediment cores: solid symbols). Surface currents and undercurrents are marked. Dashed line indicates the location of the echosounder profile in Figure 3.9.

The prevailing south-easterly trade winds drive coastal upwelling of cold and nutrient rich water originating from depths of 200-300 m in the body of the South Atlantic Central Water [*Shannon*, 1985]. Upwelling of these nutrient rich water masses leads to high productivity resulting in high concentration of photoactive pigments in surface waters (Figure 3.2a).

Upwelling in the Benguela system occurs in a number of distinct upwelling cells, which form at locations of maximum wind stress curl and where there is a change in orientation of the coastline [*Lutjeharms and Meeuwis*, 1987; *Shannon and Nelson*, 1996]. Upwelling events are strongest, most frequent and extend furthest offshore at the Lüderitz cell centred at 27°S.

Productivity is also high on the Walvis Plateau (near 19°S) and near Walvis Bay (22°S) [*Lutjeharms and Meeuwis*, 1987; *Summerhayes et al.*, 1995b]. However, there is some disagreement

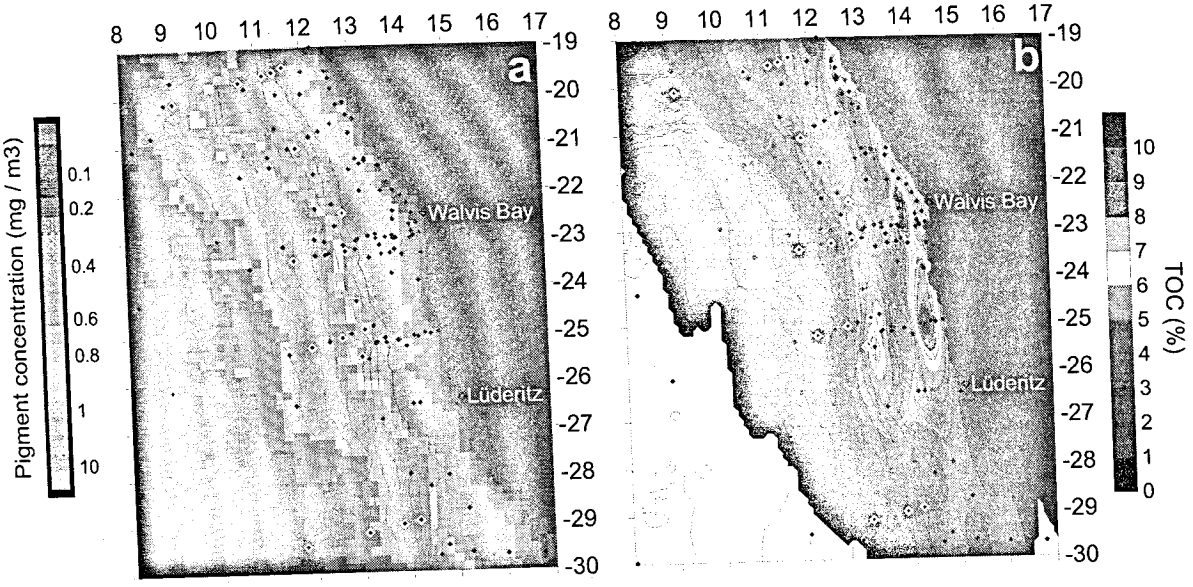

Figure 3.2. a) Mean phytoplankton pigment concentration of surface water (CZCS, November 1978 – June 1986). b) Map of TOC content of modern surface sediments from the shelf and continental slope off Namibia. The 0.1 by 0.1 degree grid was kriged with an anisotropy of 3 at 100° and a search ellipse with radii of 4.5° and 1.5°. The 150 m (red) and the 400 m (yellow) depth contours are highlighted. Surface sediment sample sites (black symbols) and core sites with TOC MAR data are marked (white symbols).

between the different authors whether the high productivity at Walvis Bay results from upwelling as stated by *Lutjeharms and Meeuwis* [1987] or whether the physical requirements for upwelling, such as wind stress, are not given in the area [*Shannon*, 1985]. The Namaqua upwelling cell located at around 29°S is less intense and smaller in size than the northern ones (Figure 3.2a).

Between 18°S and 34°S, a longshore thermal front coincident with the shelf break demarcates the seaward extent of the upwelled water (Figure 3.3). This front is highly convoluted and often disturbed by filaments and eddies, sometimes extending as far as 1300 km offshore [*Summerhayes et al.*, 1995b]. On the offshore side of the front, secondary upwelling may occur. It has been noted that enhanced phytoplankton productivity often occurs not in the centre of upwelling cells but rather offshore and at the borders of or just outside upwelling sites [*Lutjeharms and Stockton*, 1987, and references therein]. Therefore, the development of an extensive and highly convoluted field of filaments, eddies, and thermal fronts, as can be found offshore Lüderitz, is favourable for high productivity.

A poleward undercurrent has been reported for the shelf and the upper slope off Namibia [*Shannon and Nelson*, 1996] and can be modelled to follow the shelf break using a time-

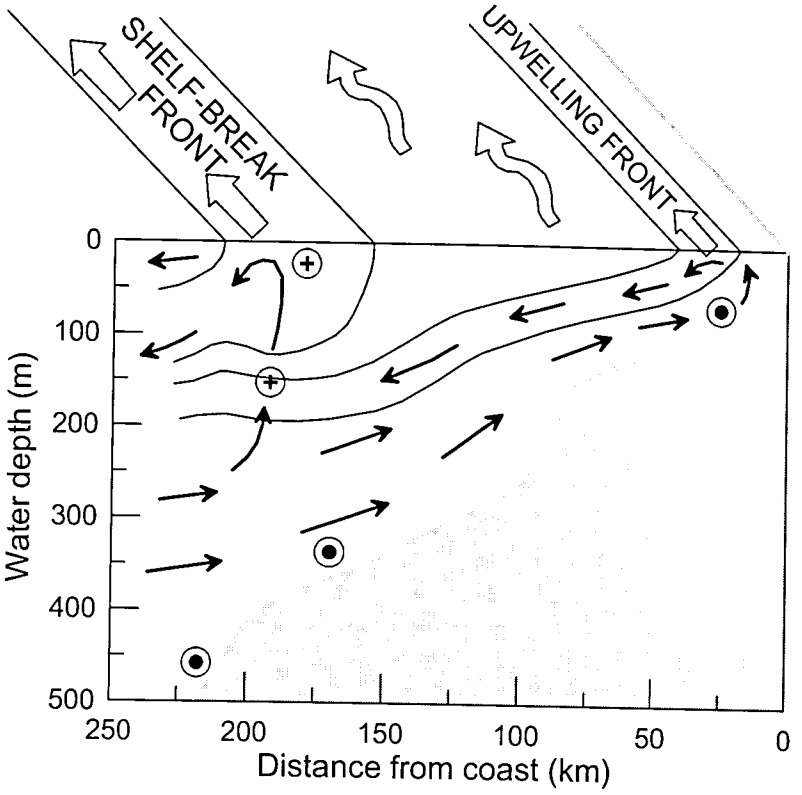

Figure 3.3. Conceptual model of upwelling off Namibia, showing cross-shelf flow, isotherms, surface currents and undercurrents moving poleward (dots in circles) and equatorward (crosses in circles) (modified after *Summerhayes* et al. 1995a,b).

dependent, wind- and density driven physical model [*Fennel,* 1999, *Skogen*, 1999]. The shelf circulation is conceptualised in Figure 3.3.

Occasional bergwinds perpendicular to the coast are the dominant means of transport for terrestrial material in the prevailing arid climate. Insignificant relative contributions of terrigenous particles to total fluxes were observed in sediment traps [*Wefer and Fischer*, 1993; *Giraudeau et al.*, 2000]. Terrestrial input, in particular of organic matter, can therefore be considered to be of minor importance in the area, which is also confirmed by $\delta^{13}C_{org}$ exhibiting consistently marine values for surface sediments [*Fischer et al.*, 1998].

3.4 Material and Methods

First we investigated the modern distribution of TOC in surface sediments from the continental shelf and slope. In a second step we calculated modern TOC accumulation on the continental shelf using published data for cores from the shelf plus new data, and modern

TOC accumulation on the continental slope based on data from sediment cores. Those sediment cores from the slope were then used for the comparison of Holocene and glacial TOC accumulation rates.

Table 3.1. Core locations, parameters used for stratigraphy, and references.

Core	Latitude (°N)	Longitude (°E)	Water depth (m)	Cruise	Parameters used for stratigraphy	Reference stratigraphy & data
GeoB1704-4	-19.407	11.612	398	M20/2	$\delta^{18}O$ planktic, carbonate	this study
GeoB1705-1	-19.505	11.398	642	M20/2	carbonate	this study
GeoB1706-2	-19.562	11.175	980	M20/2	^{14}C, $\delta^{18}O$ planktic	*Little et al.* 1997, this study
GeoB1707-1	-19.690	10.657	1232	M20/2	$\delta^{18}O$ planktic, carbonate, $U^{K'}_{37}$	this study
GeoB1028-5	-20.104	9.186	2209	M6/6	$\delta^{18}O$ planktic, carbonate, $U^{K'}_{37}$	*Müller et al.* 1997
ODP 175-1082A	-21.094	11.821	1279	ODP Leg 175	$\delta^{18}O$ planktic	*Jahn et al.* submitted
226920-3	-22.449	12.358	1683	M48/2	^{14}C, $\delta^{18}O$ benthic	*Mollenhauer et al.*, subm.
GeoB1710-3	-23.432	11.698	2987	M20/2	$\delta^{18}O$ benthic	*Kirst et al.* 1999
GeoB1711-4	-23.315	12.377	1967	M20/2	^{14}C, $\delta^{18}O$ benthic	*Kirst et al.* 1999
GeoB1712-4	-23.257	12.808	998	M20/2	$\delta^{18}O$ planktic, carbonate, $U^{K'}_{37}$	*Kirst et al.* 1999
GeoB3718-10	-24.895	13.161	1350	M34/2	colour reflectance, carbonate	this study
GeoB3720-3	-25.068	12.666	1995	M34/2	colour reflectance, carbonate	this study
GeoB3722-2	-25.250	12.021	3506	M34/2	^{14}C, $\delta^{18}O$ benthic	this study
GeoB3606-1	-25.467	13.083	1785	M34/1	^{14}C, $\delta^{18}O$ planktic	this study
ODP 175-1084A	-25.514	13.028	1991	ODP Leg 175	$\delta^{18}O$ planktic	this study, Donner pers. c
GeoB1719-7	-28.927	14.178	1010	M20/2	carbonate, dry bulk density	this study
GeoB1720-4	-29.000	13.828	1997	M20/2	dry bulk density, TOC	this study
GeoB1721-7	-29.168	13.082	3044	M20/2	$\delta^{18}O$ benthic	this study
GeoB1722-1	-29.450	11.750	3973	M20/2	$\delta^{18}O$ benthic	this study
NAM1	-22.667	14.000	120	BENEFIT/1.	^{14}C	*Struck et al.* in press
GeoB3607-2	-23.888	14.333	97	M34/1	^{14}C	this study

3.4.1 Sediment samples

The surface sediment data set used in this study consists of 137 samples, 106 of which have been published [*Lochte et al.*, 2000; *Schmiedl et al.*, 1997] and are available from the data archive PANGEA (www.pangaea.de/ddi?datasetid=53229 and /ddi?datasetid=53139). The remaining core top data are available from the same data archive (www.pangaea.de/ddi?datasetid=59873). Sampling locations are given in Figure 3.1.

The 18 gravity cores used in the time slice reconstruction were retrieved during various cruises with RV *Meteor* between 1988 and 2000 [e.g. *Schulz et al.*, 1992], one sediment core was retrieved on a cruise with RV *Petr Kottsov* in 1997, two ODP cores are from leg 175 [*Wefer et al.*, 1998]. The cores were taken on four cross-slope transects and at positions in-between the

transects. The core transects are located on the Walvis Plateau at about 19°S, offshore from Walvis Bay at about 23°S, offshore and north of Lüderitz at about 25°S, and at about 29°S. The transects will be referred to as Walvis Plateau, Walvis Bay, Lüderitz and Namaqua, respectively. Core locations and water depths are given in Table 3.1 and shown in Figure 3.1.

The sediment cores were sampled in 5 cm intervals and TOC contents of all samples were measured according to standard procedures. Details are given in the references listed in Table 3.1. The stratigraphic framework of the sediment cores from the slope is based on core-to-core correlation along the transects. Cores with particularly well-constrained age control were considered the reference for the respective transect. From these cores, which ideally have ^{14}C datings as well as benthic stable oxygen isotope stratigraphies, correlations were made to the neighbouring cores on the transects including parameters such as carbonate contents, alkenone $U^{K'}_{37}$ and spectrophotometer colour reflectance data. Parameters used for the establishment of age control of the individual cores are also listed in Table 3.1. An example for correlation along the transect located at ~23°S (Walvis Bay) is presented in Figure 3.4 and described in the following.

Based on the radiocarbon datings and the benthic oxygen isotope record, the age control of GeoB1711 is considered most reliable out of the three cores on the transect. A reservoir correction of -0.4 kyr was applied to all radiocarbon datings. For the core levels below 400 cm corresponding to ages older than the range of reliable radiocarbon dating, the age model is based on visual correlation with the normalised SPECMAP standard record [*Imbrie et al.*, 1984] identifying isotopic events. Besides, the interval of the last glacial maximum is identified as the period of heaviest benthic oxygen isotope values and assigned an age of 16.1 - 19.5 ^{14}C years following *Mix et al.* [2001].

The age model for GeoB1710 is based on peak-to-peak correlation of the *C. wuellerstorfi* oxygen isotope record to that from GeoB1711. A very good match between the two cores can be achieved spanning the last 135 ka and is also evident in the records of $CaCO_3$, TOC and SST. Below 663 cm core depth, the level corresponding to 135 ka, we adopt the stratigraphy for GeoB1710 from *Bickert and Wefer* [1999].

The oxygen isotope record of the planktic foraminiferal species *G. bulloides* in core GeoB 1712 is very variable and does not allow unambiguously identifying isotopic events. However, a good match between cores can be achieved by using other sediment parameters. This is deduced from the fact that the correlation of GeoB1710 and GeoB1711 based on benthic foraminifera isotope records results in a good match between the $U^{K'}_{37}$- and $CaCO_3$-records. Thus, a multi-parameter correlation, primarily based on $U^{K'}_{37}$ and $CaCO_3$ and supplemented

by the TOC-data, was performed for GeoB1712. A best match for all parameters including $\delta^{18}O$ in all three cores was sought.

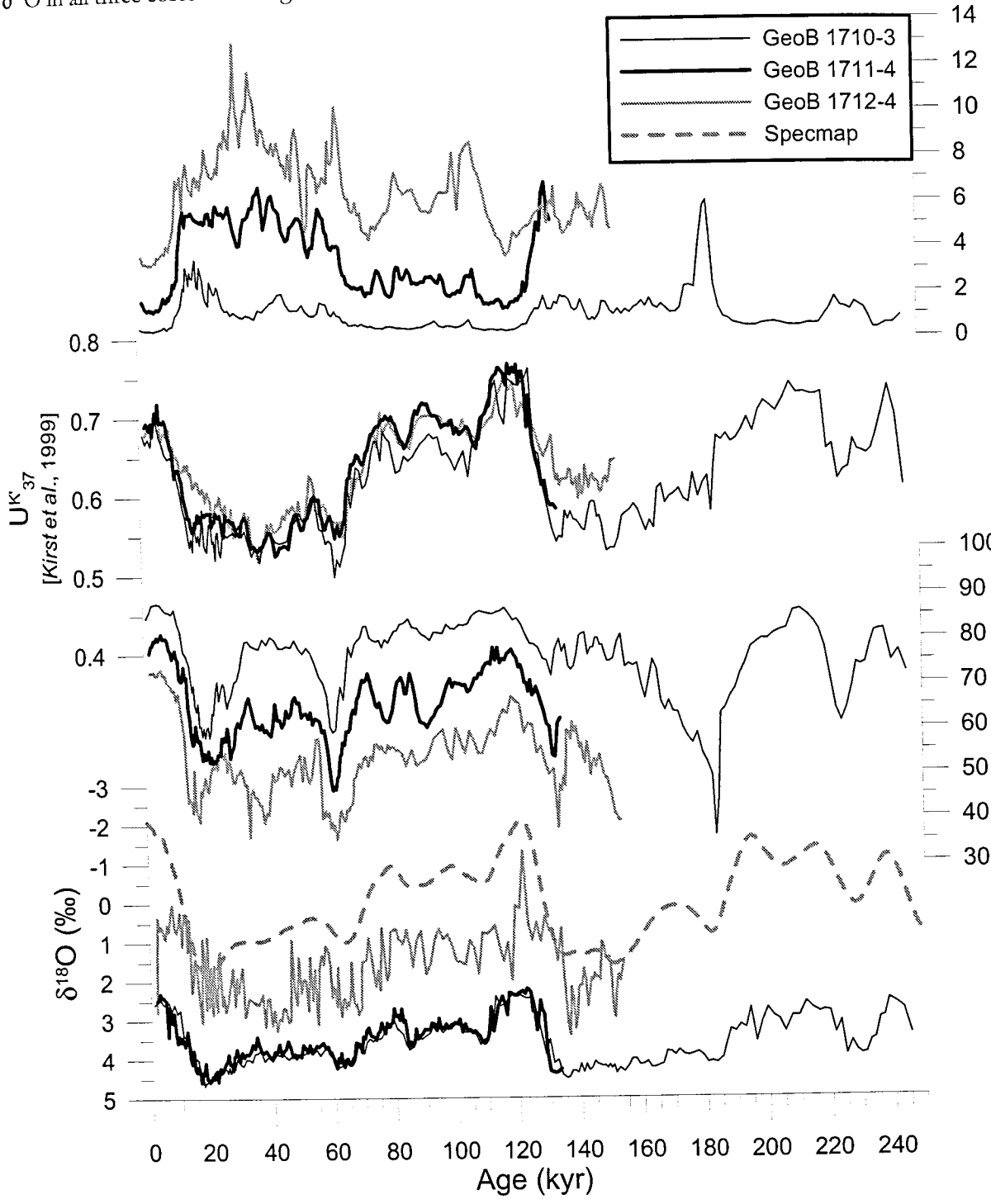

Figure 3.4. Stratigraphically correlated sedimentary records from cores GeoB1710-3 (thin black line), GeoB1711-4 (thick black line) and GeoB1712-4 (grey line) located on the cross-slope transect off Walvis Bay (~23°S).

For each of the sediment cores from the slope, core depths corresponding to calendar ages of 4 - 8 kyr (containing the Holocene climate optimum period) and 19 - 23 kyr (16.1 – 19.5 ^{14}C kyr; Last Glacial Maximum (LGM)) were identified. The Holocene climate optimum (referred to as Holocene) interval was chosen in order to avoid errors in the time slice comparison due to incomplete early diagenetic alteration of surface sediments and uncertainties of core top age, and in order to compare equal time intervals at both time slices (4 kyr each).

From the age models, sedimentation rates for each core were determined by linear interpolation of the age in between tie points. Mean TOC contents, mean dry bulk density (DBD) and mean sedimentation rates were calculated for each time interval and each core. TOC MAR were derived by multiplying TOC contents of the samples, DBD and sedimentation rate and expressed as gram carbon per square-meter and year (g C $m^{-2}yr^{-1}$). The main factor influencing the calculation therefore is the sedimentation rate. Core depth, TOC %, DBD, sedimentation rate and resulting TOC mass accumulation rates (MAR) are given in Table 3.2.

For the surface sediment samples, neither measured DBD nor sedimentation rates are available. Modern TOC MAR were thus estimated using TOC contents of surface sediments and assuming DBD and sedimentation rates within the ranges observed in the sediment cores from the shelf and the upper slope for the Holocene sections.

Table 3.2: (next page) Depth and age ranges for Holocene and LGM time slices and corresponding core data

Core	Age range (^{14}C kyr)	Depth range (m)	Mean DBD (g cm^{-3})	Mean TOC (%)	Sed.Rate (cm kyr^{-1})	TOC MAR (g C m^{-2} yr^{-1})
GeoB1704-4	4.35-7.42	0.38-0.63	0.66	2.9	8.0	1.5
	16.1-19.2	1.48-1.73	0.79	1.7	8.1	1.1
GeoB1705-1	4.28-8.1	0.33-0.83	0.59	3.5	13.1	2.7
	18.6	1.88	0.49	5.8	1.7	0.5
Geob1706-2	4.33-7.66	0.03-0.33	0.52	3.5	9.0	1.6
	16.12-19.22	1.13-1.43	0.49	5.8	9.7	2.7
GeoB1707-1	4.4-8.1	0.33-0.68	0.53	3.0	9.4	1.5
	16.1-19.1	1.43-1.63	0.50	5.1	6.6	1.7
GeoB1028-5	4.2-8.2	0.23-0.43	0.82	0.3	5.0	0.1
	16.8-19.0	0.83-0.93	0.71	1.2	3.8	0.3
ODP 175-1082A	6.7	0.67	0.58	2.9	12.3	2.0
	19.0	2.17	0.52	5.5	9.9	2.8
226920-3	4.3-7.7	0.38-0.93	0.58	2.7	16	2.5
	16.4-19.4	2.13-2.58	0.51	6.4	16.7	5.5
GeoB1710-3	4.9-7.7	0.23-0.38	0.74	0.4	5.3	0.2
	16.1-19.3	0.83-1.18	0.47	2.7	10.9	1.4
GeoB1711-4	4-8	0.23-0.63	0.68	1.3	10.0	0.9
	16.1-19.25	1.48-1.83	0.51	5.4	11.1	3.1
GeoB1712-4	4.5-8.2	0.23-0.53	0.58	3.4	8.0	1.6
	16.3-19.4	1.23-1.53	0.50	6.8	9.7	3.3
GeoB3718-10	4.3-7.6	0.03-0.28	0.51	4.6	7.7	1.8
	16.1-19.4	0.93-1.38	0.40	8.2	13.8	4.5
GeoB3720-3	4.4-7.8	0.18-0.53	0.67	1.3	10.5	0.9
	16.3-19.2	1.43-1.73	0.39	6.2	10.4	2.5
GeoB3722-2	4.2-8.2	0.08-0.28	0.72	0.43	5.2	0.2
	16.9-19.8	0.68-0.83	0.35	3.4	4.9	0.6
GeoB3606-1	6.7-7.9	0.03-0.33	0.50	4.7	18	4.2
	16.2-19.6	3.18-3.88	0.48	6.5	21.6	6.7
ODP 175-1084A	4-8	0.97-1.92	0.48	5.5	24.1	6.2
	16.2-19.4	4.40-5.50	0.47	7.7	33.7	11.9
GeoB1719-7	3.9-7.7	0.28-0.53	0.80	1.3	6.5	0.7
	16.4-19	1.03-1.18	0.84	1.2	5.8	0.6
GeoB1720-4	4.8-7.2	0.18-0.28	0.82	0.8	4.0	0.26
	17.1-18.4	0.68-0.73	0.76	0.9	4.0	0.28
GeoB1721-7	4-7.5	0.08-0.18	0.80	0.2	2.9	0.05
	16.25-19.3	0.43-0.53	0.69	0.5	3.5	0.12
GeoB1722-1	4.3-7	0.03-0.08	0.80	0.2	1.9	0.03
	18	0.33	0.64	0.2	1.9	0.03
GeoB3607-2	4.00-6.40	1.53-4.23	0.27	6.8	60	10.3
NAM1	0.125-3.09	0-5.445	0.3	5	166	24.9

3.4.2 Regionalisation

In order to calculate regional organic carbon budgets for the study area, the respective data from individual sites were interpolated to derive maps of the regional distribution of modern day surface sediment TOC contents and of TOC MAR for the Holocene and LGM time slices. When attempting a mass accumulation budget of an area, it has to be taken into account that latitude and longitude are not equally spaced co-ordinates. The lateral distortion increases with latitude. The study area ranges across 11 degrees of low to moderate latitude, where the distortion is relatively small. Therefore, we ran the interpolation using latitude and longitude co-ordinates, but for the budgets, the area of each grid cell was calculated with the appropriate latitudinal length.

A 0.1 by 0.1 degree grid was calculated for modern TOC distribution on the continental shelf and slope, for Holocene TOC MAR and for LGM TOC MAR on the slope. The kriging method [*Davis*, 1986] was used with an anisotropy factor of 3 along a preferential direction of 100°, roughly parallel to the shelf break. The major and minor radii of the search ellipse were set to 4.5° and 1.5° respectively. In this way the calculation of grid node values for areas where data coverage is very poor is avoided.

3.5 Results and Discussion

3.5.1 Modern distribution of high productivity and of sedimentary total organic carbon

In Figure 3.2b, a map of surface sediment TOC content for the shelf and upper continental slope off Namibia is given. A belt of high TOC contents extends parallel to the coast, coincident with the diatomaceous mud belt described by *Bremner* [1983]. Within this belt, three distinct areas of high TOC content can be distinguished, one each at the Walvis Plateau, at Walvis Bay and north of Lüderitz. All of the maxima on the shelf occur where very high surface water productivity is observed (Figure 3.2a) and correspond to high productivity cells at these three sites as described above. Moreover, the dominant maximum in TOC content occurs at Lüderitz, where strongest and most persistent upwelling is reported to take place. It is noteworthy, however, that the high surface water productivity observed at the Namaqua cell is not preserved in surface sediments. It has to be taken into account that the spatial resolution in that area is low. One possible explanation may be that in the southern sub-system, most of the production is regenerated production, even though total production in both sub-systems is nearly equal [*Brown et al.*, 1991]. TOC content in surface sediments in the entire southern half of the Benguela system has been reported to be lower than in the

northern half [*Shannon*, 1985], which is a further indication that different productivity regimes prevail in the North and in the South. If this is the case, the TOC content of inner shelf sediments seems to be an accurate proxy for export productivity and thus for new production related to nutrient import via upwelled water.

Additional maxima in surface sediment TOC content are observed on the upper slope offshore from Lüderitz, centred at 25.5°S and a minor one on the Walvis Plateau. These maxima occur below sites of high surface water productivity as observed in satellite images and could be related to jets and eddies inducing high productivity at offshore sites. The sediments on the upper continental slope offshore from Walvis Bay, where satellite images suggest the productivity to be as high as at the other sites, are not as rich in organic carbon as both to the North and South. That the upper slope TOC maximum off Walvis Bay lacks in spite of the high near-shore productivity could imply that, and be explained if, true upwelling does not occur and offshore filaments and jets do not develop at 23°S as stated by *Shannon* [1985]. As an alternative explanation, a shelf break front with a related maximum in productivity has been suggested by *Summerhayes et al.* [1995b], which could account for the development of upper slope TOC maxima. If a shelf break front exists, downwelling would occur on its shoreward side. The downwelling water masses could potentially transport plankton and suspended particles and in this way promote particle sinking and sedimentation. However, such a feature cannot be identified on satellite derived productivity maps. Another possible mechanism for the development of distinct upper slope maxima may be downslope transport of TOC rich material from the shelf. From observations of suspended matter in surface and subsurface water over the continental slope, *Summerhayes et al.* [1995b] concluded that some of the material reaching the slope must be re-suspended shelf sediments instead of reflecting the surface water productivity at the respective sites. They estimate the relative importance of re-suspended shelf sediments to be at maximum 20 % of the total deposited material. Deposition on the slope would occur where dynamic conditions prevent further erosion, i.e. in morphologic depressions.

If export productivity were the only controlling factor of sediment TOC content, a gradient towards lower values with increasing distance to the coast should be recorded in the sediments. Instead, low TOC contents are observed on the entire outer shelf, which is where poleward undercurrents occur as conceptualised in Figure 3.3. They may cause winnowing and focusing of fine-grained, TOC rich sediment particles in deposition centres at sites less exposed to the currents, e.g. morphologic lows. Therefore it seems likely that the low TOC content in the outer shelf surface sediment is related to winnowing of the fine fraction

containing most of the organic matter by the observed poleward undercurrents. Alongshore undercurrents, which are reported to be stronger in the Southern part of the system than in the North [*Shannon and Nelson*, 1996], could provide an alternative explanation for the low TOC contents in surface sediments on the shelf near the Namaqua cell. However, the

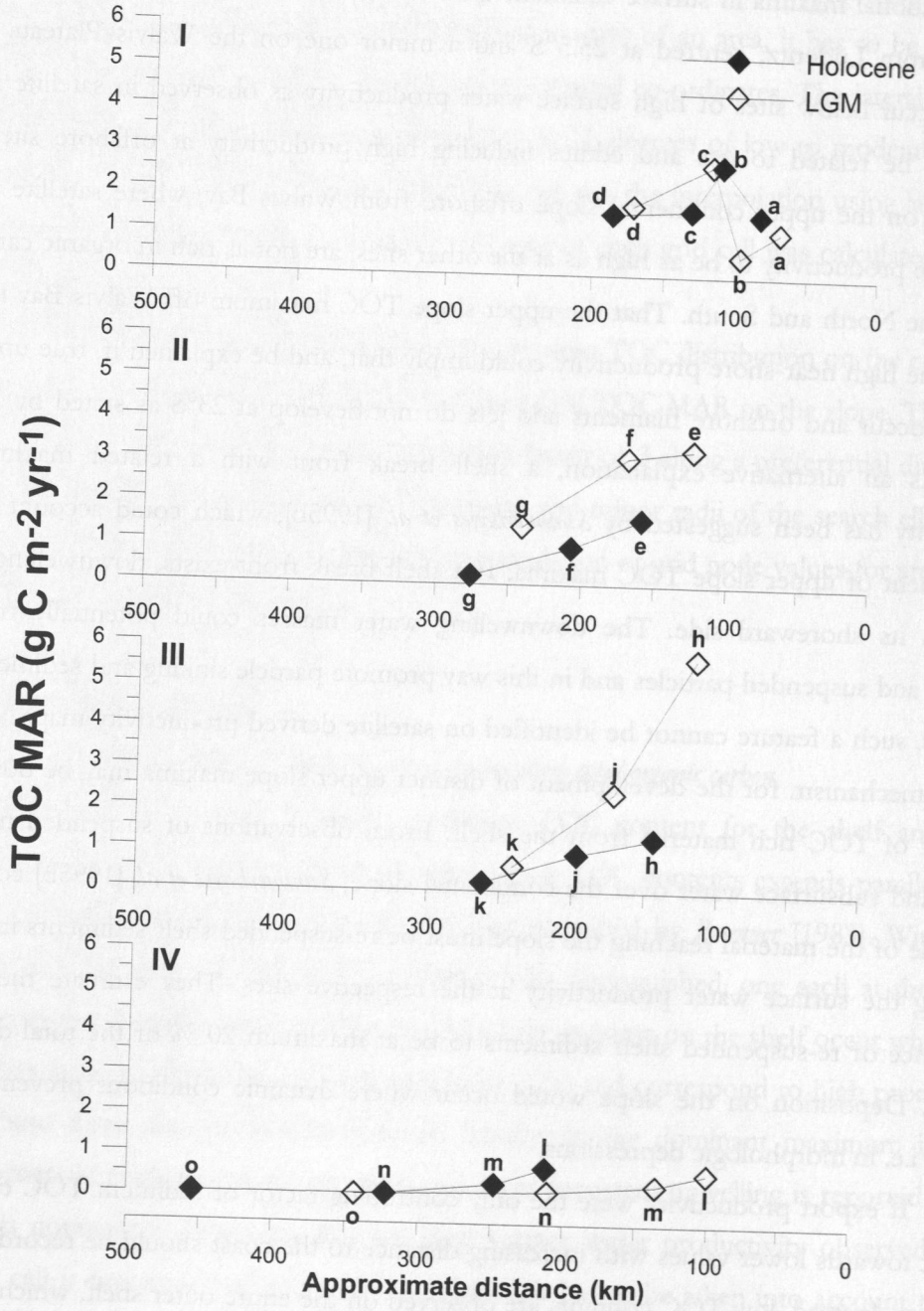

Figure 3.5. TOC MAR for the four down-slope core transects investigated from North (top) to South (Walvis Plateau – I; Walvis Bay – II; Lüderitz – III; Namaqua – IV). Solid symbols refer to TOC MAR calculated for the Holocene, plotted versus distance of the core sites to the modern coastline. Open symbols refer to TOC MAR calculated for the LGM, plotted versus distance to the 120 m isobath. (a – GeoB1704-4, b – GeoB1705-1, c – GeoB1706-2, d – GeoB1707-1, e – GeoB1712-4, f – GeoB1711-4, g – GeoB1710-3, h – GeoB3718-10, j – GeoB3720-3, k – GeoB3722-2, l – GeoB1719-7, m – GeoB1720-2, n – GeoB1721-7, o – GeoB1722-1).

sediments there are rather muddy [*Shannon*, 1985], which indicates that currents are relatively weak.

Winnowing of sediments on shelves is a well known phenomenon and has been described e.g. for the continental slopes of the Middle Atlantic Bight [*Biscaye and Anderson*, 1994] and the Bay of Biscay [*Heussner et al.*, 1999]. Current induced control of the sedimentation processes has also been proposed for the Northwest African upwelling system by *Diester-Haass and Müller* [1979] and *Martinez et al.* [1999]. However, the overall role of undercurrent induced sediment erosion and re-deposition on outer shelf deposits is not well understood today, and further research is necessary.

From the modern distribution of TOC in sediments underlying the Benguela high productivity system, two main controls on the TOC flux into the sediment become evident: the site and intensity of surface water productivity and current activity. During the glacials, the high productivity cells may have migrated offshore due to sea-level regression. These possible changes can be investigated on the continental slope, since from the slope sediment cores covering a longer time range are available, and offshore displacement of high productivity cells would result in enhanced productivity at these sites.

3.5.2 Total organic carbon mass accumulation rates during the Holocene and the Last Glacial Maximum

In Table 3.2, all calculated TOC MAR are given as well as the core depth ranges corresponding to the Holocene and LGM time slices, the mean DBD of the sediment, the mean TOC content and the sedimentation rate used in the calculation. On Figure 3.5 TOC MAR of the core sites are plotted versus their approximate distance to the present day coastline for Holocene samples and versus their approximate distance to the 120 m isobath for glacial samples to account for glacial sea-level, which was lowered by about 120 m with respect to the present day sea-level [e.g. *Bard et al.*, 1990]. The coastline off Namibia and therefore the site of high productivity due to upwelling of nutrient rich waters must have been displaced seaward by 10-30 km at the northern three transects and by up to 110 km at 29°S. More importantly, however, the shelf areas may have been too shallow for coastal upwelling cells to develop due to the lowered glacial sea-level. This would cause the sites of upwelling to be displaced even further off-shore.

At the northernmost cross-slope transect on the Walvis Plateau, this way of plotting the TOC MAR shows the offshore displacement of the site of maximum accumulation during sea-level lowstand. During both the Holocene and the LGM, very similar TOC MAR of between 1.1 and 2.7 g C m^{-2} yr^{-1} are observed at similar distances to the respective coastline. In

contrast to the other transects, highest accumulation rates here do not occur at the core site in the shallowest water depth and closest to the shore, but rather at the deeper sites GeoB1705-1 (Holocene) and GeoB1706-2 (LGM). The very low value of 0.5 g C $m^{-2} yr^{-1}$ for the LGM at site GeoB1705-1 is noteworthy.

On the core transect off Walvis Bay, a similar cross-slope gradient is observed for the two time slices, but TOC MAR is increased during the LGM at all sites. Holocene values range from 0.2 to 1.6 g C $m^{-2} yr^{-1}$, while glacial TOC MAR ranges between 1.4 and 3.3 g C $m^{-2} yr^{-1}$.

This glacial increase is even stronger on the Lüderitz transect, but here the upslope increase in accumulation of organic matter was greater during the LGM. Holocene TOC MAR between 0.2 and 1.3 g C $m^{-2} yr^{-1}$ are observed and increase to 0.6 to 5.7 g C $m^{-2} yr^{-1}$ during the LGM. The maximum glacial TOC MAR value calculated for the slope in this study (11.9 g C $m^{-2} yr^{-1}$) occurred at site ODP 175-1084A also off Lüderitz, but this core site is not located on one of the cross-slope transects and therefore is not shown on Figure 3.5.

At the Namaqua transect , TOC MAR are relatively low compared to the sites of high accumulation at 25°S, and no significant increase nor a change in the general pattern is observed when comparing Holocene and LGM sediments. The rather large glacial displacement of the shoreline does not strongly affect the accumulation rates at the respective core sites. It must be noted, however, that the core sites on this transect are further away from the coast and at deeper water depths than on the other core transects. As data from closer to the coast are missing, we may not draw an authentic picture of TOC MAR in the southern part of the study area. The cores taken at great distances from the coast may not be influenced strongly by upwelling but rather reflect open ocean conditions. Flux of organic matter to the sea-floor is also a function of water depth [e.g. *Betzer et al.*, 1984], which may be part of the reason why little TOC accumulates at these deep sites.

A large portion of the differences between Holocene and LGM TOC MAR can be explained by the influence of the glacial 120 m sea-level drop on the position of the high productivity cells. On the Walvis Plateau cross-slope transect, the site of maximum TOC accumulation is situated at a constant distance to the respective coastline during both the Holocene and the LGM. We interpret this as an off-shore displacement of the centre of high productivity during the LGM. The very low TOC MAR at site GeoB1705-1, however, may be caused by current activity and will be discussed later.

On the two core transects off Walvis Bay and off Lüderitz, the presumed offshore migration of the high productivity centre is less evident from the distribution of TOC accumulation. As

can be seen in Figure 3.5, accumulation of organic carbon is increased at all core sites during the LGM. The rates of increase are higher than what would be expected if the sites of high productivity during the LGM were simply displaced seaward by the same distance as was the shoreline. When considering the similarity of modern day productivity patterns and modern surface sediment TOC content distribution, the relative increase in accumulation of organic matter on the continental slope with respect to the shoreline (Figure 3.5) may be attributable to increases in glacial productivity at the respective sites and would demand increased upwelling favourable winds during the LGM. Stronger glacial winds and an increase in rates of upwelling have been proposed for the Benguela area by several authors [*Summerhayes et al.*, 1995b; *Schneider et al.*, 1995; *Little et al.*, 1997a, b; *Lavik*, 2001]. Seaward displacement of the site of upwelling of nutrient rich surface water leading to high productivity in the Walvis Bay area has also been proposed by *Lavik* [2001], who deduced such a process from comparison of stable nitrogen isotope records ($\delta^{15}N$) of the Walvis Bay core transects investigated in this study, and by *Bertrand et al.* [in press] for a core near Lüderitz. Another explanation for the high relative increase in TOC MAR could be that the sites of production were displaced further seaward than was the shoreline, making the upper slope core sites during the LGM more proximal to the upwelling cells than during the Holocene. In that case, an overall increase in glacial productivity would not be required. In order to compare upper slope spatial distribution of centres of TOC MAR between the Holocene and glacial conditions, maps must be derived from the transect data for the Holocene and LGM time slices.

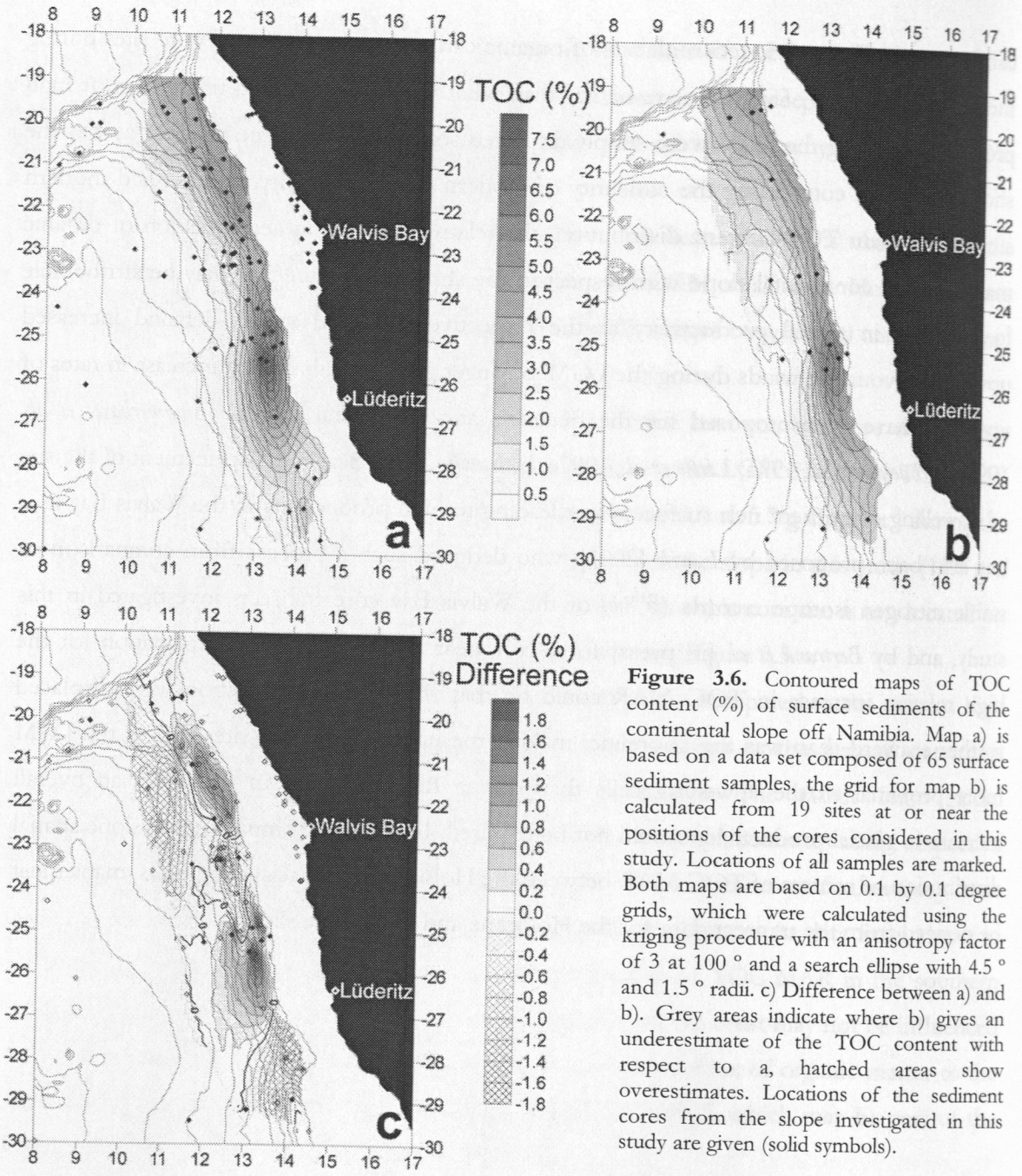

Figure 3.6. Contoured maps of TOC content (%) of surface sediments of the continental slope off Namibia. Map a) is based on a data set composed of 65 surface sediment samples, the grid for map b) is calculated from 19 sites at or near the positions of the cores considered in this study. Locations of all samples are marked. Both maps are based on 0.1 by 0.1 degree grids, which were calculated using the kriging procedure with an anisotropy factor of 3 at 100 ° and a search ellipse with 4.5 ° and 1.5 ° radii. c) Difference between a) and b). Grey areas indicate where b) gives an underestimate of the TOC content with respect to a, hatched areas show overestimates. Locations of the sediment cores from the slope investigated in this study are given (solid symbols).

3.5.3 Reliability of the interpolation procedure

Holocene and LGM TOC MAR data are only available for 19 sites on the continental slope. It needs to be tested whether this limited data set will nevertheless allow making statements on the regional distribution pattern of TOC accumulation on the continental slope by interpolating the data. The reliability of the interpolation was tested by comparing the gridded results of two different data sets of surface sediment TOC weight percent from the continental slope off Namibia. We used a subset of the surface sample data set from Figure

3.3 for this purpose, containing all of the samples from the slope (n=65). From this data set, a reduced data subset (n=19) was derived, consisting of surface data from sampling locations at or near the sites of the cores considered in this study.

From Figure 3.6 it is evident that both data sets yield comparable regional distribution patterns of TOC weight percent in surface sediment samples. However, differences between the two maps appear in some areas. The largest differences occur in areas without coverage in the small data set, e.g. at latitudes between 20°S and 21°S, and at the margins of the study area. The grid based on the small data set has a tendency to smoothen the variability of the regional distribution and does not show the extreme values, but the deposition centres still are visible. Even though the second data set does not have a good spatial resolution, the general features are evident. Moreover, a comparison of the total integral of both maps (Figure 3.7) shows that both data sets result in similar values. On the other hand, this clearly demonstrates how incomplete the set of available sediment cores still is with respect to the small scale features in TOC distribution in surface sediments and in the modern productivity patterns.

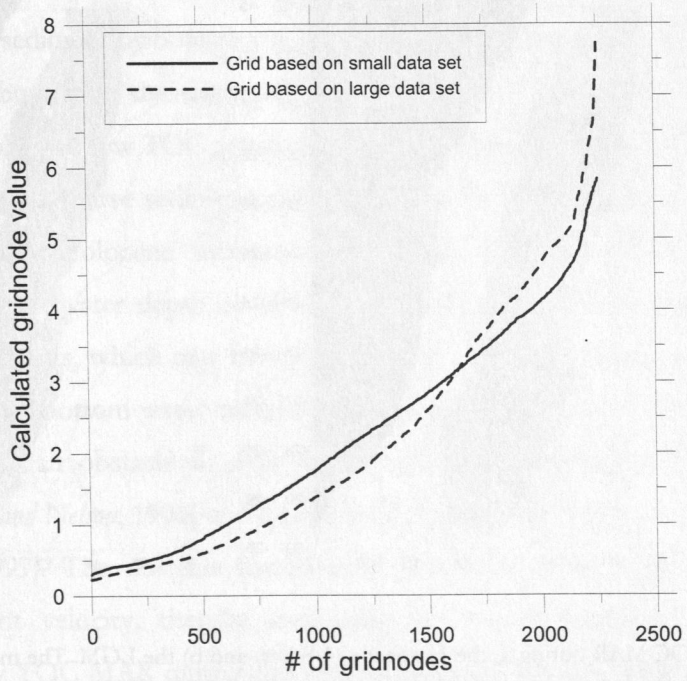

Figure3.7. Sorted grid node values (TOC content) calculated for maps 5 a) (dashed) and 5 b) (black). (The graphs are plotted in analogy to a hypsographic curve of e.g. elevation). Note that variations observed in 5 a) tend to be levelled out in 5 b) and the maximum values are not observed, but the integral of both maps is about the same.

The best overall correlation between the grids produced from the two data sets using different interpolation algorithms is achieved with the kriging procedure. Therefore, we used

this method for calculation of Holocene and LGM distribution of TOC content and TOC MAR.

3.5.4 Regional distribution of organic carbon accumulation during the Holocene and the Last Glacial Maximum

Figure 3.8 shows maps of the regional distribution of TOC MAR for the Holocene and the LGM on the continental slope off Namibia. For both time slices, the dominant maximum in TOC accumulation occurs north of Lüderitz (25 - 26°S). This feature has already appeared on the map of TOC weight percent in surface sediments (Figure 3.3), which is based on a larger data set. Therefore, we consider this maximum a true feature, but its exact boundaries cannot be determined from the data set available. Additionally, TOC MAR is increased in the vicinity of the Lüderitz upwelling cell during the LGM. This is also true for the area offshore from Walvis Bay.

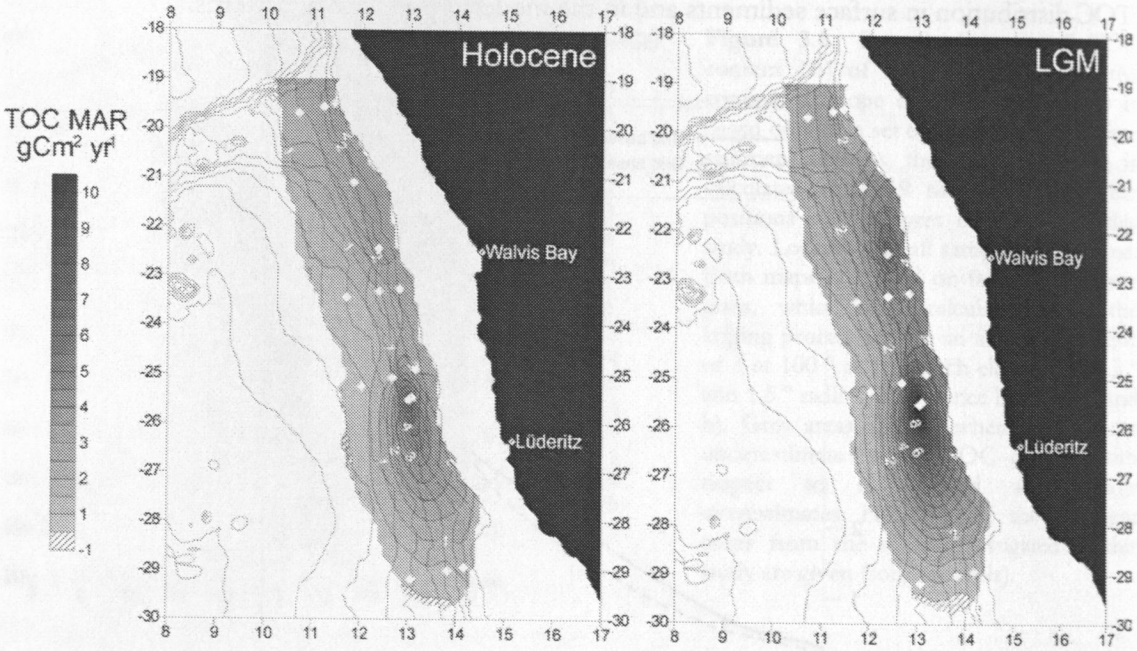

Figure 3.8. Maps of TOC MAR during a) the Holocene (4-8 kyr) and b) the LGM. The maps are based on grids calculated as described for Figure 3.5. Hatched areas are negative grid values and represent artefacts of the gridding algorithm.

As discussed above, our data indicate a glacial increase in productivity in response to stronger upwelling as a possible reason for the observed increase in TOC accumulation, but we do not believe that the glacial increase of export productivity is the only factor that influences TOC MAR in the slope sediments.

Increased terrestrial input during the LGM may also lead to increased TOC accumulation. Despite the observation of an increase in pollen abundance in glacial sediments with respect to the Holocene core sections (L. Dupont, University of Bremen, personal communication) we consider the terrestrial input of organic matter to be insignificant for the total mass balance. The main reason is the carbon isotopic composition of organic matter displaying marine values (around -20‰) throughout the whole cores [P. J. Müller; University of Bremen, unpublished]. The dominant means of transport of terrestrial material to the Namibian continental margin is wind, and there is no evidence for wetter climate in Southern Africa during the LGM [*Partridge et al.*, 1999]. Aeolian dust collected off Northwest Africa within the Saharan dust plume is reported to contain less than 1 weight % organic carbon [*Lavik*, 2001]. Namibian desert dust is expected to have a similar organic/inorganic ratio as Saharan dust. Sediments off Namibia often contain 10 – 20 weight % organic carbon and thus cannot be composed to a significant fraction of terrigenous material, even though the total amount of dust input to the area was probably increased in response to stronger trade winds, which was also suggested by *Hinrichs et al.*, [1999].

Transport of sediment by bottom water currents is another potential process influencing the sediment distribution on the slope off Namibia. A good example is the Walvis Plateau transect. Here we observe low TOC accumulation rates at shallow water depth (GeoB1704-4) together with relatively coarse sediment in the upper few cm of the core [*Schulz et al.*, 1992], corresponding to the Holocene section. This indicates that at present the sedimentary environment at 400 m water depth on the Walvis Plateau is characterised by deposition of coarse grained sediments, which may be an effect of currents. The particular susceptibility of this site to erosion by bottom water currents could be explained by the local bathymetry. The Walvis Ridge forms an obstacle to near shore, poleward undercurrents which have been observed [*Shannon and Nelson*, 1996] and can be modelled for water depths of about 200 m and deeper [*Skogen*, 1999]. The obstacle results in a reduction of flow diameter and thus an increase of current velocity, thereby increasing its erosive potential. We attribute the observation of low TOC MAR during the Holocene at site GeoB1704-4 (ca. 400 m modern water depth) to this effect. During the LGM, TOC MAR at the adjacent but deeper site GeoB1705-1 (ca. 640 m modern water depth) is even lower than the Holocene TOC MAR at GeoB1704-4. The site of maximum erosion would have remained at a similar distance to the coast and at a similar water depth during the LGM with respect to the Holocene, and the erosive potential of the current may have increased as a function of current velocity. For water depths of 1200 to 1800 m, sediment waves are observed and have been attributed to a contour

current in the area south of the Walvis Ridge [*von Lom-Keil*, 2001]. This contour current seems to have been stable during the past 5 Ma, as the sediment waves can seismically be observed in old stratigraphic units.

Further south on the continental slope in water depths around 1500 m, sediment echosounder data from the high-resolution 4 kHz Parasound system reveal a complex pattern of areas of high sediment accumulation in morphological lows and areas of very low accumulation or erosion on elevated parts of the sea floor (Figure 3.9). The echosounder section on this Figure was recorded on a ship track parallel to the shelf break. It illustrates the high lateral heterogeneity of the sedimentary environment also parallel to the coast, with zones of truncated seismic reflectors suggesting erosion on elevated parts of the sea-floor and zones of deposition in morphologic depressions. Obviously, the bottom morphology combined with erosive bottom water currents has a significant influence on the sediment distribution.

When postulating stronger winds for the LGM, the physical consequence may be an increase in strength of the poleward undercurrent on the outer shelf, as indicated by the observations on the Walvis Plateau. This hypothesis should be tested by physical oceanographic modelling. If the bottom water currents on the upper slope strengthen analogously in response to stronger winds, an even greater current induced impact on the sedimentation pattern for the LGM has to be taken into account resulting in stronger sediment focusing in morphological lows.

The influence of bottom water currents combined with heterogeneous regional distribution of the productivity has important implications concerning the potential to derive system scale information from an individual core. Not only does the combined effect of the productivity gradient and increasing water depth with increasing distance to the coast result in variable sedimentation patterns perpendicular to the coast, additional variability related to bottom morphology and current activity has to be considered in directions parallel to the coast. Even for a relatively large set of cores as we used in this study, the limitations of resolving small-scale regional variability are evident (compare Figure 3.6). Small-scale regional variability in sediments observed in neighbouring cores is a common feature. Individual cores are not necessarily representative of the whole area. The complex pattern of sedimentation with deposition centres can only be investigated with a very large number of cores representing the various sedimentary environments. Changes in surface and deep-water circulation in the area can likewise only be inferred from data from a number of sampling sites.

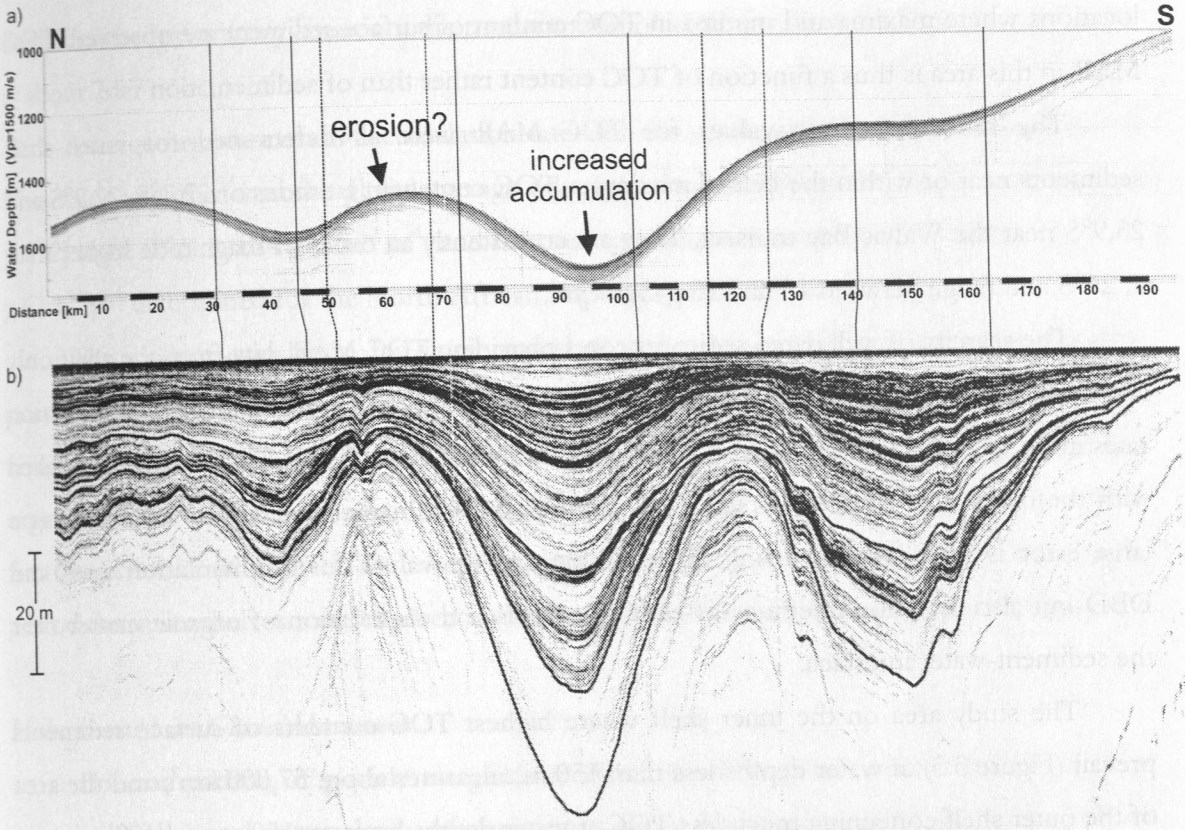

Figure 3.9. Sediment echosounder profile parallel to the coast of Namibia (for location see Figure 3.1). The bottom morphology evident from the normal Parasound echosounder profile (top panel) is characterised by distinct hills and troughs. Sediment thicknesses are higher in the morphologic depressions as evident from the bottom panel, which is a Parasound section normalised to the sea floor. Slopes facing north have lowest sediment thicknesses and may be sites of erosion.

Nevertheless our data set allows deriving better qualitative and quantitative information about changes in the spatial distribution of productivity centres and the budget of TOC accumulation, respectively, than was known before for the Namibian upwelling region.

3.5.5 Carbon Budgets

Modern total organic matter accumulation

Seven values for modern TOC MAR on the shelf have been determined [*Vetrov et al.*, 1996; *Struck et al.*, in press; this study]. Four of these data points are located on a cross-shelf transect at about 25°S. This transect crosses the distinct inner shelf maximum in surface sediment TOC content, where surprisingly low TOC MAR were calculated (between 0.08 and 1.03 g C m^{-2} yr^{-1}) [*Vetrov et al.*, 1996], and maxima and minima in TOC MAR occur at the same

locations where maxima and minima in TOC content of surface sediment are observed. TC MAR in this area is thus a function of TOC content rather than of sedimentation rate.

The remaining three values for TOC MAR were all determined for inner she sediments near or within the belt of maximum TOC content at latitudes of 22.7°S, 22.9°S ar 23.9°S near the Walvis Bay transect. They are consistently an order of magnitude higher tha at 25°S and range between 10 and 25 g C m^{-2} yr^{-1}.

The scarcity of well dated sediment cores providing TOC MAR data from the shelf onl allows us to estimate a budget for the modern situation by assuming average sedimentatio rates and dry bulk densities for the inner and outer shelf areas. These can then be multiplie with the observed surface sediment TOC content. Such a budget is relatively uncertain, as large error is introduced not only by assuming average values for sedimentation rates an DBD but also by ignoring effects of early diagenesis and degradation of organic matter nea the sediment-water interface.

The study area on the inner shelf where highest TOC contents of surface sediments prevail (Figure 3.3) at water depths less than 150 m, measures about 57,000 km^2, and the area of the outer shelf containing much less TOC at water depths between 150 m and 400 m water depth covers about 91,000 km^2. When assuming average dry bulk density of 0.3 g cm^{-3} and 0.5 g cm^{-3} for the inner and outer shelf areas respectively, ranges for modern TOC accumulation can be determined. For the inner shelf area, calculated total modern organic carbon accumulation ranges from 4.2 x 10^{11} g yr^{-1} to 1.3 x 10^{12} g yr^{-1} corresponding to average sedimentation rates of 50 cm kyr^{-1} and 150 cm kyr^{-1} respectively. For the outer shelf, total organic carbon accumulation is estimated to range between 8.5 x 10^{10} g $yr^{-1}$and 8.5 x 10^{11} g yr^{-1} (sedimentation rates of 5 and 50 cm yr^{-1}). For the total shelf area this adds up to minimum and maximum values of TOC accumulation of 5 x 10^{11} and 2.15 x 10^{12} g C m^{-2} yr^{-1} respectively. These values correspond to 0.6 and 2.8 % of total annual carbon production for the area calculated by *Brown et al.* [1991], suggesting a high percentage of carbon burial. *Wollast* [1998] estimated 3.3 % of total production carbon to be buried on the continental shelves, supporting our maximum estimate for TOC accumulation on the Benguela shelf.

In order to estimate the modern TOC accumulation on the continental slope at water depths of more than 400 m, we calculated total TOC accumulation using the DBDs and sedimentation rates determined for the Holocene time slice (4 – 8 kyr) and surface sediment TOC content. For the slope area of approximately 243,000 km^2, total accumulation is about 3.2 x 10^{11} g C yr^{-1}. If the maximum estimate for the modern shelf accumulation accurately

describes the present day situation, the modern ratio of shelf versus slope TOC accumulation is about 7:1.

Average organic carbon accumulation rates for the whole slope are about 1.3 g C m^{-2} yr This value is higher than the global average organic carbon burial rate estimated by *Reimers et* [1992] to be 0.96 ± 0.24 g C m^{-2} yr^{-1}, and is in very good agreement with TOC MAR of 1.1 – 1 g C m^{-2} yr^{-1} determined for the North African slope by *Müller and Suess* [1979].

This budget calculation for slope and shelf sediments reveals that by far the greater portion of organic carbon accumulation today is taking place on the shelf. This confirms the results of *Berner* [1982, 1992] and *Wollast* [1998], who have pointed out that most of the organic matter accumulates close to the continents. It has important implications, however, for the estimate of glacial TOC accumulation in the Benguela system, during which time period the inner shelves were exposed and for which we lack data from the outer shelves.

Holocene and Last Glacial Maximum

For comparison of glacial/interglacial budgets, we did not use surface values. Instead, we calculated annual accumulation of organic carbon for the time interval between 4 and 8 kyr based on the maps for Holocene accumulation of organic matter on the continental slope off Namibia at water depths of more than 400 m, in order to reduce the probability of errors introduced due to less diagenetic degradation of TOC in surface sediments than in the glacial core sections.

An approximate accumulation of 3.1 x 10^{11} g C yr^{-1} for the Holocene was calculated, which is only slightly less than what was calculated for the slope using surface sediment values. For the LGM, an approximate accumulation of 5.7 x 10^{11} g C yr^{-1} was calculated. This corresponds to an84 % increase in organic carbon accumulation during the LGM with respect to the Holocene. The largest difference between LGM and Holocene TOC mass accumulation is observed north of Lüderitz in the area where maximum accumulation occurs during both time periods and where greatest rates of upwelling and highest productivity are observed today (Figure 3.10a). TOC accumulation there increased only by a factor of 1.5 to 2 (Figure 3.10b), while highest factors of increase are observed at the more offshore sites reflecting the seaward displacement of the centres of high productivity during the LGM. In contrast, TOC accumulation remained constant or was lower during the LGM than during the Holocene on both the northern (Walvis Plateau) and the southern margins of the study area. Average organic carbon accumulation rates for the whole slope were 2.5 g C m^{-2} yr^{-1} during the LGM.

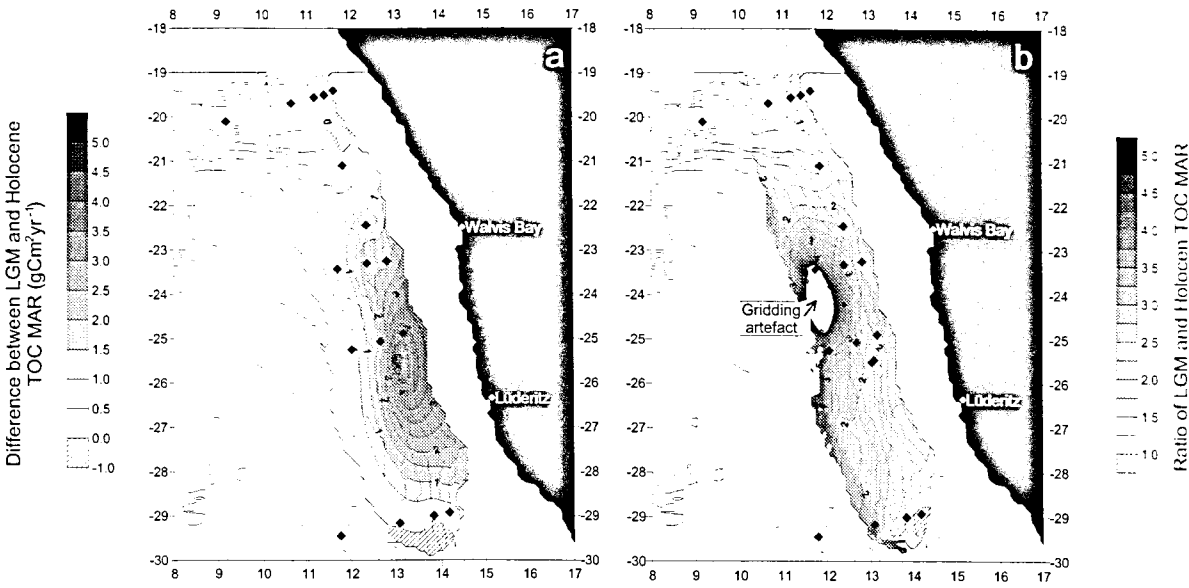

Figure 3.10. a) Difference between the two maps in Figure 3.8 (b) – a)). Grey areas highlight where TOC MAR was higher during the LGM than during the Holocene, hatched areas indicate a Holocene increase over the LGM value. b) Factors of increase in TOC MAR during the LGM, hatched areas mark glacial decreases of TOC.

The area exposed during sea-level lowstand, which was not available for sediment deposition under LGM conditions, represents about 40 % of the total shelf area. It is at the same time the area, where presently more than 80% of the TOC accumulation takes place. We have no data on glacial accumulation of TOC on the outer shelf, so speculative assumptions have to be made. One scenario requires that the present situation with no accumulation on the outer shelf prevailed during the LGM. The glacial increase of TOC MAR observed on the slope is too small to balance the modern accumulation on the shelf. Thus total accumulation of organic matter in the area would have been decreased by between 30% and 77% (based on the minimum and maximum estimates of modern TOC accumulation respectively). An alternative scenario would be to extrapolate to the shelf our observation made on the slope of an ~80 % glacial increase in TOC accumulation and assume further that in contrast to the modern situation, the outer shelf was a deposition area during the LGM. This would require the currents observed there today to not have been active during the LGM, allowing for deposition of fine-grained organic rich material on what today is the outer shelf. Then shelf TOC accumulation for the LGM based on the estimated accumulation for the present day situation can be calculated. The assumed increase in organic carbon accumulation (+ 80 %) would then balance the loss in deposition area (- 40%), so that the total accumulation of organic matter on the Benguela shelf would have been increased only slightly during the LGM with respect to the Holocene. The effects of the drop in sea-level and the increase in accumulation due to increased productivity effectively "cancel out". However, this is only

possible due to the specific morphology of the Benguela system with its wide and relatively deep shelf.

With the data available in this study it is not possible to judge whether these scenarios are realistic. Detailed investigation of the outer shelf areas would be necessary. The fate of the organic matter that may have been deposited on the inner shelf during a previous interglacial period is not clear either. If it was eroded while exposed or during the deglacial sea-level rise, the material must have been transported to the sea and probably has been deposited on the slope. Thus associating patterns of accumulation with a certain time period is difficult, and so is reconstruction of paleoproductivity.

3.5.6 Contribution to global Carbon Cycle

Our TOC budgets calculated for the slope sediments and the estimates of the shelf contribution indicate that modern annual accumulation of organic carbon in sediments of the Benguela upwelling system is at maximum about 2.5 x 10^{12} g C, while the glacial estimate is at maximum 2.9 x 10^{12} g C (increased accumulation on the outer shelf (2.37 x 10^{12} g C) plus increased accumulation on the slope of 5.7 x 10^{11} g C), if the scenario involving deposition on the outer shelf is considered. On glacial/interglacial time-scales, the difference in organic carbon burial thus is relatively small. The results of *Frank et al.* [2000] for the Southern Ocean had similar implications. They observed constant overall export productivity over glacial/interglacial time-scales with a shifting locus of deposition in response to the migration of oceanic fronts. Assessing the total contribution to atmospheric CO_2 reduction made by the biological productivity in the Benguela system would require quantification of the changes in carbonate chemistry mediated by input of organic matter. *Bertrand et al.* [in press] have shown that carbonate dissolution and preservation is the main controlling factor for organic carbon concentration in sediments off Namibia. Budgeting carbonate dissolution for the area, however, would require further assumptions and is beyond the scope of our study.

The increase in glacial organic carbon accumulation observed in the Benguela upwelling system may not be representative for all of the mid and low latitude South Atlantic, as the high productivity caused by coastal upwelling represents a special case. The calculated budgets show that organic carbon accumulation in the Benguela area is large compared to other ocean areas [cf. *Berner*, 1982] indicating that upwelling systems account for a significant fraction of global organic carbon burial. Thus the fact that a glacial-interglacial increase in the Benguela system would be relatively small, if it exists at all, may imply that overall organic carbon burial was not significantly increased during the LGM.

3.6 Conclusions

- The deposition pattern in the Benguela upwelling systems records high productivity as well as current activity, which controls deposition of material by the interaction of currents and morphology of the shelf and slope.

- Due to strong heterogeneity on small lateral distances, it is only possible to make detailed statements on budgets and the general characteristics of an upwelling system when using sets of sediment cores from all the different sedimentary environments within the system. Even a set of 19 well-dated sediment cores is not enough to resolve small scale variability.

- Upwelling cells were displaced in a seaward direction in response to sea-level lowstand during the last ice age.

- The shelf area in the Benguela upwelling system receives most of the modern accumulation of organic material. Budgets of organic carbon accumulation in the oceans have to consider the shelves as the main area of deposition, including morphology of the shelves and effects related to sea-level changes.

- Total mass accumulation of organic material on the continental slope, reflecting export production and offshore displacement of the upwelling cells, has increased by up to 84 % during the LGM in the Benguela upwelling system.

- Budgeting accumulation of organic carbon in LGM and Holocene sediments from the Benguela upwelling system shows that burial of organic matter, taken without its implications for deep ocean chemistry, involves only small amounts of carbon. The observed changes imply a glacial enhancement of the biological productivity in surface waters.

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Asynchronous alkenone and foraminifera records from the Benguela Upwelling System

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4.1 Abstract

Radiocarbon stratigraphy is an essential tool for high resolution paleoceanographic studies. Age models based on radiocarbon ages of foraminifera are commonly applied to a wide range of geochemical studies, including the investigation of temporal leads and lags. The critical assumption is that temporal coupling between foraminifera and other sediment constituents, including specific molecular organic compounds (biomarkers) of marine phytoplankton, e.g. alkenones, is maintained in the sediments.

To test this critical assumption in the Benguela upwelling area, we have determined radiocarbon ages of total C_{37}-C_{39} alkenones in 20 samples from two gravity cores and three multicorer cores. The cores were retrieved from the continental shelf and slope off Namibia, and samples were taken from Holocene, deglacial and Last Glacial Maximum core sections. The alkenone radiocarbon ages were compared to those of planktic foraminifera, total organic carbon, fatty acids and fine grained carbonates from the same samples. Interestingly, the ages of alkenones were 1000 to 4500 years older than those of foraminifera in all samples.

Such age differences may be the result of different processes: Bioturbation associated with grain size effects, lateral advection of (recycled) material and redeposition of sediment on upper continental slopes due to currents or tidal movement are examples for such processes.

Based on the results of this study, the age offsets between foraminifera and alkenones in sediments from the upper continental slope off Namibia most probably do not result from particle-selective bioturbation processes. Resuspension of organic particles in response to tidal movement of bottom waters with velocities up to 25 cm/s recorded near the core sites is the more likely explanation.

Our results imply that at sites influenced by either one of these processes, age control established using radiocarbon measurements of foraminifera is inadequate for the interpretation of alkenone-based proxy data. Observed temporal leads and lags between foraminifera based data and data derived from alkenone measurements may therefore be

secondary signals, i.e. the result of processes associated with particle settling and biological activity.

4.2 Introduction

Molecular level studies of organic compounds from marine sediments can provide useful information on past and present oceanic environments. In particular, one suite of marine biomarkers, the long-chain unsaturated ketones ("alkenones") produced by certain haptophyte algae contain valuable information on paleo sea surface temperatures (SSTs) [e.g. *Brassell et al.*, 1986; *Müller et al.*, 1997]. Reconstructing SSTs by measuring the unsaturation ratio of C_{37}- alkenones is robust, rapid, and inexpensive, requires small samples and is applicable in most oceanographic settings [e.g. *Prahl et al.*, 1988, *Müller et al.*, 1998]. Thus the alkenone parameter is now widely used and largely established as a paleoceanographic proxy. Furthermore, combining proxy information derived from alkenones and isotopic composition of calcareous nanno- and microfossils can help deducing more detailed information on past ocean surface conditions, such as estimates of paleosalinities [*Rostek et al.*, 1993; *Lamy et al.*, 2002]. Another application of a combination of such proxy records is to disentangle the timing of variations in ocean temperature relative to changes in sea-level and continental ice volume [*Schneider et al.*, 1995; *Kirst et al.*, 1999; *Rühlemann et al.*, 1999; *Bard et al.*, 2000; *Herbert et al.*, 2001; *Kim et al.*, 2002]. The underlying assumption all these investigations is that temporal coupling between the different signal carriers is maintained upon deposition and burial in the sediments. This is a prerequisite which may not be met under certain conditions. In particular, physical processes associated with sedimentation and burial of different constituents after signal formation in the surface waters have been proposed to cause difficulties [e.g. *Sachs et al.*, 2000]. In contrast, chemical alteration of the alkenone paleotemperature signal through degradation is generally regarded to be minor (see review by *Grimalt et al.* [2000]).

Examples for physical processes are sediment mixing and advection, both of which can smooth the various proxy records. Through bioturbation, apparent temporal offsets between paleoclimate proxies may be produced [e.g. *Hutson*, 1980; *Bard et al.*, 1987; *Broecker et al.*, 1999; *Bard*, 2001]. Sediment constituents that differ in size, shape, density and composition may be subject to differential mixing. The attenuation and apparent temporal offset of a signal is inversely proportional to the sedimentation rate [*Guinasso and Schink*, 1975; *Bard et al.*, 1987; *Brown et al.*, 2000; *Anderson*, 2001]. Intensity and depth of bioturbation, however, are hard to measure directly, and depend among other factors on benthic food supply [*Trauth et al.*, 1997].

In addition to potentially inducing temporal offsets, advection of allochthonous material may carry an alkenone signature that does not reflect SST variations in the overlying waters

[*Benthien and Müller*, 2000]. SST estimates which strongly deviate from the surface signal are observed in areas with high resuspension fluxes [*Thomsen et al.*, 1998]. Vertical and horizontal transport processes may affect the different types of sediment particles to varying extents [e.g. *Brown et al.*, 2000; *Thomsen and Gust*, 2000; *Bard*, 2001]. Therefore, successful coupling of faunal and isotopic data from calcareous fossils with alkenone measurements and other proxies based on the organic matter fraction requires verification that the different sediment constituents are coeval.

Paleoceanographic research is increasingly focused on high accumulation rate sites, as rapidly accumulating sediments facilitate the formation and preservation of high resolution records. Such sites include deep-sea drift deposits, basin depocenters or continental margins underlying high productivity regions (e.g., coastal upwelling areas). While lateral advection of sediments is believed to be the cause for the build-up of pelagic drift bodies, at continental margin sites most of the material accumulating on the slopes is assumed to derive from proximal sources. In either case, however, allochthonous materials associated with the diluent may potentially carry signals that are spatially and temporally decoupled from those derived from overlying waters.

Independent dating of alkenones and calcareous microfossils in sedimentary records is required in order to assess the validity of the coupling of paleoenvironmental information from these two phases [*Sachs et al.*, 2000]. For late Pleistocene and Holocene deposits, radiocarbon dating is the common tool in paleoceanographic studies. In such studies, radiocarbon ages of foraminifera have been most extensively used. Where foraminiferal ^{14}C measurements are impractical (either due to low abundance or poor preservation), bulk organic carbon (OC) has been used as an alternative [e.g., *Jansen et al.*, 1984; *Summerhayes et al.*, 1995]. However, the latter is generally considered less reliable because of the potential for contamination by pre-aged or relict terrigenous OC [e.g., *Marsiello and Druffel*, 1998]. However, recent advancements of AMS dating techniques now permit determination of radiocarbon ages of biomarkers such as alkenones or sterols on a compound-specific or compound-class level [*Eglinton et al.*, 1997; *Pearson et al.*, 1998].

Continental margins are key locations for high temporal resolution studies. Foraminiferal ^{14}C dating in these locations is often problematic due to dissolution of the calcite tests in organic rich sediments. Likewise ^{14}C dating of bulk OC may be problematic because the proximity of continental land masses means that terrigenous OC may be a significant component. Since waters overlying the margins are often productive and preservation of organic matter is high, the availability of a molecular equivalent to the foraminifera impervious to terrigenous influence and effectively preserved in continental

margin sediments (e.g., alkenones) is an attractive alternative for developing sediment chronologies.

In order to investigate the temporal relationship between alkenone derived SST records and oxygen isotope data from planktic foraminifera we applied this new technique of molecular ^{14}C analysis to sediments from the Benguela upwelling system off Namibia. For comparison of absolute ages, we performed a series of radiocarbon measurements of total organic carbon, alkenones and co-occurring planktic foraminifera. We found significant age offsets between the different forms of carbon in sediments from the upper continental slope both during the Holocene and the Last Glacial periods. These results illustrate the limitations of developing coupled alkenone foraminiferal proxy sediment records in coastal upwelling systems.

4.3 Study Area

The Benguela upwelling system off Namibia is one of four major coastal upwelling systems on eastern boundaries of the world's oceans (Figure 4.1). Persistent SE trade winds result in upwelling of nutrient rich subsurface waters. Upwelling is perennial but occurs in distinct cells along the coasts of Namibia and South Africa, and in events that vary seasonally in strength and duration. High rates of biological productivity are induced by this continuous supply of nutrients, and sediments rich in organic carbon accumulate at high rates on the continental shelf and slope [*Lutjeharms and Meeuwis*, 1987; *Shannon*, 1985; *Shannon and Nelson*, 1996]. Input of terrigenous organic matter is minor, due to the arid climatic conditions in the adjacent continental areas. The dominant means of transport from the land is by wind, there are no perennial rivers, and land vegetation is sparse.

Today, a well defined belt of soft sediment with organic carbon (OC) contents up to 20% (dry wt.) is observed between approximately 19° and 26°S on the inner shelf around 100 m water depth [*Bremner*, 1983]. Sedimentation rates in this area are locally as high as ca. 170 cm/kyr [*Struck et al.*, in press]. This near-shore area is also characterised by extensive sea-floor hypoxia and anoxia and formation of sulfidic sediments [*Weeks et al.*, 2002]. OC contents in surface sediments are low on the outer shelf and increase again on the upper continental slope with maximum values of up to 8% near the principal upwelling cell off Lüderitz (25°S) at around 1500 m water depth [*Mollenhauer et al.*, in press; Chapter 3]. Bottom water on the upper continental slope contains sufficient oxygen to support benthic life, however. Sedimentation rates on the upper continental slope range from 5 to 20 cm/kyr. Vigorous bottom currents over the outer shelf [*Shannon and Nelson*, 1996] likely exert a strong influence on the sedimentation of fine-grained particles and associated organic matter. Similar currents are

probably active on the upper continental slope. Sedimentation rates and OC contents are positively correlated and are greatest in topographic depressions protected from bottom water currents [*Mollenhauer et al.*, in press; Chapter 3].

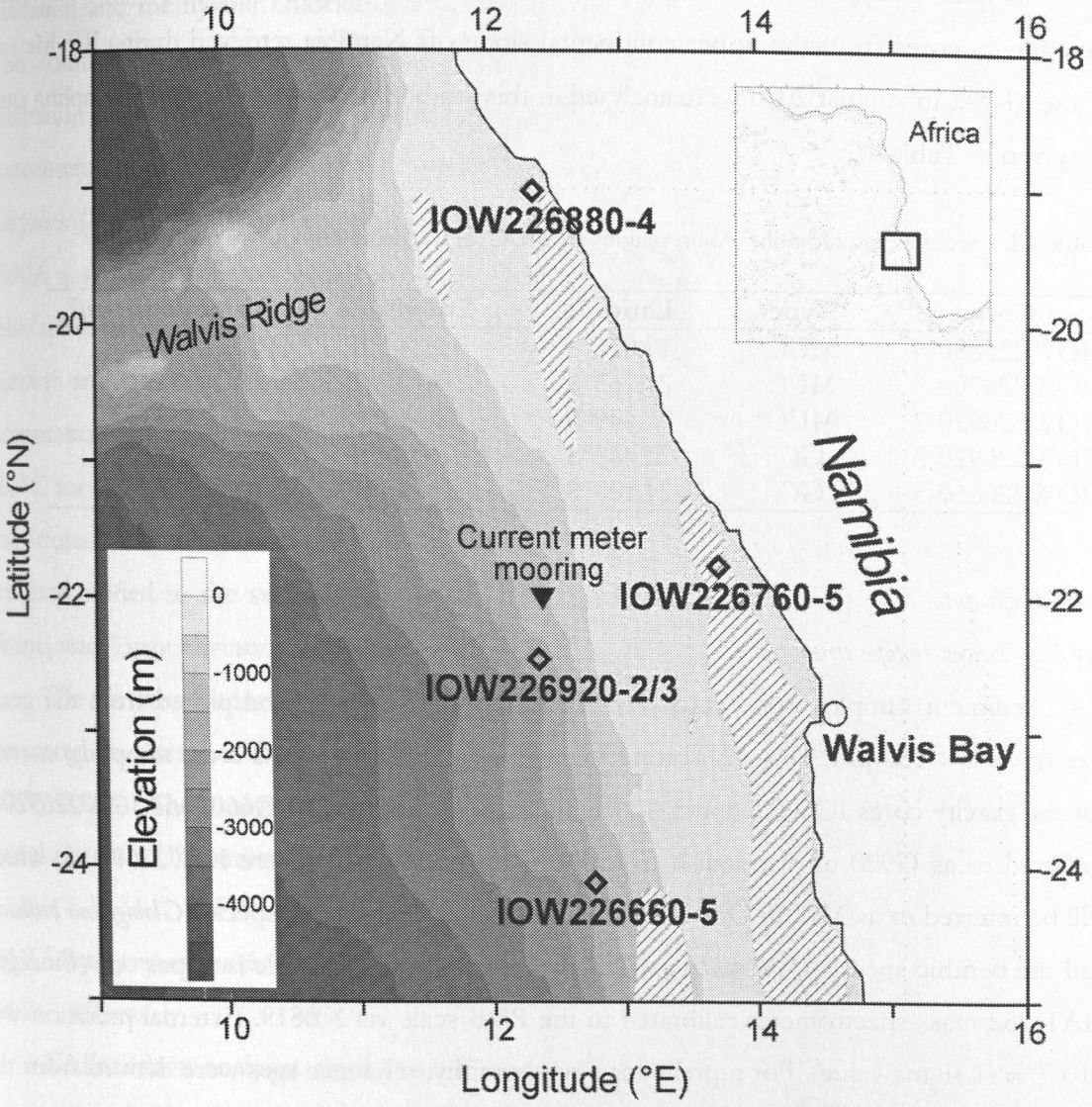

Figure 4.1. Study area and core sites. In hatched areas, surface sediments contain more than 5% TOC.

Productivity in the Benguela system is considered to have been higher during the Last Glacial Maximum (LGM) [e.g. *Summerhayes et al.*, 1995; *Hinrichs et al.*, 1999]. Sediment cores covering this period are, however, only available from the continental slope where sedimentation rates were generally higher than during the Holocene [*Mollenhauer et al.*, in press; Chapter 3]. Similarly, OC contents are generally higher in glacial than in Holocene sediments. Part of this increase may be related to seaward displacement of upwelling centres as a result of the lowered sea-level during the glacial period. Bottom currents may likewise have been active

at a more seaward position, and evidence of current influence can be deduced from the glacial sedimentation pattern as well [*Mollenhauer et al.*, in press; Chapter 3].

4.4 Materials and Methods

Samples from two multicorer cores from the continental shelf and one multicore and two gravity cores from the upper continental slope off Namibia retrieved during RV Meteor cruise M48-2 in August 2000 were analysed in this study (Figure 4.1). Details of sampling sites are given in Table 4.1.

Table 4.1. Core sites and locations. Abbreviations are MUC for multicore and GC for gravity core.

Core	Type	Latitude	Longitude	Water depth [m]
IOW226880-4	MUC	19.016°S	12.344°E	98
IOW226760-5	MUC	21.763°S	13.723°E	94
IOW226920-2	MUC	22.449°S	12.358°E	1683
IOW226920-3	GC	22.449°S	12.358°E	1683
IOW226660-5	GC	24.108°S	12.765°E	1821

4.4.1 Basic data

4.4.1.1 Oxygen isotope stratigraphy

Sediment samples were wet-sieved, and foraminifera were hand picked from the grain size fraction >150 μm. Oxygen isotope analyses were performed in a 5 cm sampling interval for the gravity cores IOW226660-5 (in the following referred to as G660) and IOW226920-3 (referred to as G920 to distinguish from the corresponding multicore IOW226920-2, which will be referred to as M920). One sample series each of the planktic species *Globigerina bulloides* and the benthic species *Cibicidoides wuellerstorfi* were analysed for stable isotopes on a Finnigan MAT 252 mass spectrometer calibrated to the PDB scale via NBS19. External precision was ±0.07‰ (1 sigma value). For a preliminary stratigraphy, reference ages were derived from the benthic $\delta^{18}O$ record by correlation with the SPECMAP stacked signal [*Imbrie et al.*, 1984].

4.4.1.2 Bulk organic carbon and carbonate

Sediment samples for bulk analyses taken from gravity cores in 5 cm depth intervals were freeze dried and homogenized prior to processing. Total carbon (TC) and total organic carbon (TOC) were obtained by combustion at 1050°C using a Heraeus CHN-O-Rapid elemental analyzer as described by *Müller et al.* [1994]. Carbonate was calculated from the difference between total and organic carbon and expressed as calcite ($CaCO_3$ = (TC-TOC) x 8.33).

4.4.1.3 Alkenone $U^{K'}_{37}$ records

Long-chain alkenones were extracted from 0.5-1 g aliquots of freeze-dried and homogenized sediment by ultrasonication using a UP200H sonic disruptor probe (Hielscher, S3 Micropoint, 200 W, amplitude 60%, pulse 0.5 s) and successively less polar mixtures of methanol and methylene chloride (CH_3OH, CH_3OH/CH_2Cl_2 1:1, CH_2Cl_2), each for 3 min. The combined extracts were washed with demineralized water to remove sea salt and methanol, dried over Na_2SO_4, purified using a silica gel cartridge (Varian Bond Elut), concentrated under N_2, and finally taken up in 25 µl of a 1:1 CH_3OH/CH_2Cl_2 mixture. Aliquots (3 µl) of this extract were analyzed by capillary gas chromatography using a HP 5890A gas chromatograph equipped with a 60 m column (J&W DB1, 0.32 mm x 0.25 µm), split/splitless injection (1:10), and flame ionization. Helium was used as carrier gas. The injector and detector temperatures were set to 280 and 320°C, respectively, and the oven temperature was programmed from 50-250°C at 25°C min^{-1}, 250-310°C at 1.5°C min^{-1}, hold at 310°C for 26 min, 310-320°C at 30°C min^{-1}, hold at 320°C for 15 min. Quantification of di- and triunsaturated C_{37} alkenones was achieved using octacosane acid methyl ester as internal standard, added to the samples prior to extraction, the relative response factor of the C_{38} n-alkane, and Turbochrome 4 analytical software.

The alkenone unsaturation index was calculated from $U^{K'}_{37} = [C_{37:2}]/[C_{37:3} + C_{37:2}]$ and converted into temperature values applying the calibration of *Prahl et al.* [1988] ($T = (U^{K'}_{37}-0.039)/0.034$). The analytical precision based on replicates and lab-internal reference samples was about 0.01 $U^{K'}_{37}$ units, or 0.3°C.

4.4.2 Sample preparation for radiocarbon analysis

4.4.2.1 Alkenones

Radiocarbon analyses require relatively large amounts (>20 µg C) of the compound to be measured. For this purpose, a method for quantitative isolation and purification of alkenones as a compound class was applied [*Xu et al.*, 2001; *Ohkouchi et al.*, in prep.]. Sediments were stored frozen after sampling, and were freeze dried and homogenized prior to processing. In order to recover sufficient C_{36}-C_{39} alkenones, ~100 g of sediment were extracted with a Soxhlet apparatus for 48 hours using dichlormethane and methanol (93:7). The extracts were dried and saponified using 0.5M KOH in methanol (~15 mL, 80°C, 2 h). The products were extracted three times with n-hexane after the addition of distilled water. The combined extracts were brought to dryness under a stream of nitrogen. After re-dissolution in n-hexane, the compounds were separated into three fractions using small columns fitted with silica gel (200-400 mesh, 1% deactivated). Hydrocarbons were eluted with

n-hexane, ketones including alkenones with dichlomethane:hexane (2:1) and more polar compounds with methanol. From the ketone fraction alkenones were further separated and purified by urea adduction, following the protocol described by *Marlowe et al.* [1984], and $AgNO_3$-SiO_2 column chromatography. A final cleaning step with silica gel chromatography was employed to remove any remaining impurities. The resulting fraction contained only C_{36}-C_{39} alkenones with estimated purities >95%. Estimates of compound quantity were made from gas chromatographic analysis of small aliquots calibrated via an external standard (behenic acid myristyl ester). These samples were transferred into pre-combusted quartz-glass tubes, the solvent was eliminated under a stream of nitrogen, copper oxide was added, and the tubes were evacuated and flame-sealed. The samples were combusted (900°C, 5 hours), and the resulting CO_2 was purified, measured and subsequently converted to graphite by reduction over a cobalt catalyst in the presence of hydrogen for radiocarbon analysis by accelerator mass spectrometry (AMS) [*Eglinton et al.*, 1997]. Radiocarbon measurements were performed at the National Ocean Science AMS (NOSAMS) facility in Woods Hole, USA.

4.4.2.2 Fatty acids

Fatty acids were recovered from the acidic fraction of the saponified total lipid extract and converted to methyl ester derivatives (FAME) with 5% hydrochloric acid in methanol under a nitrogen atmosphere at 80°C. FAMEs were extracted with n-hexane and further purified using small silica gel columns as described above. Two fractions were collected, with the FAMEs eluting in dichlomethane:n-hexane (2:1). Purified individual FAMEs were collected using a preparative capillary gas chromatography system as described in detail by *Eglinton et al.* [1996].

A HP 5890 series II gas chromatograph, equipped with a HP 7673 auto-injector, a Gerstel CIS-3 injection system, and a Gerstel preparative trapping device was fitted with a Chrompak CP-Sil 5 CB column (100 m x 0.53 mm x 0.5 μm). The injection volume was 5 μl, and the GC temperature program was 40°C (1 min), 30°C/min to 120°C, 6°C/min to 320°C (25 min). One percent of the effluent passed through a FID and the remaining 99% were collected in a series of seven U-traps. Traps 1 – 3 were cooled (-20°C) and programmed to collect C_{14}, C_{16} and C_{18} FAMEs, traps 4 – 6 were left at room temperature and programmed to collect C_{24}, C_{26}, and C_{28} FAMEs. The content of each trap was recovered using solvent (dichloromethane), and any column bleed was removed by subsequent elution through small silica gel columns. Afterwards, FAMEs were transferred into pre-combusted quartz tubes and processed for radiocarbon analysis at NOSAMS as described above.

4.4.2.3 Bulk organic carbon

AMS radiocarbon analyses of TOC were performed using subsamples of the freeze-dried and homogenized material containing approximately 1 mg organic carbon and taken prior to lipid extraction. These were acid-treated to remove carbonates (10% hydrochloric acid, 60°C, 3 hrs and 1 hr), rinsed with distilled water until neutral and filtered on pre-combusted quartz-fibre filters. The carbonate free sediment material was transferred into pre-combusted quartz tubes, 1 mg silver and 2 g copper oxide were added, the tubes were evacuated, sealed and combusted (900°C, 5 hrs). The resulting CO_2 was purified, measured and converted to graphite over an iron catalyst in the presence of hydrogen for radiocarbon analysis at the NOSAMS facility following standard procedures [*McNichol et al.*, 1994].

Base insoluble organic matter was separated from humic acids by treating the decarbonated bulk sample with 1% sodium hydroxide (4 hrs, 60°C). The base residue was washed neutral with distilled water and once more treated with hydrochloric acid. After final neutralization with distilled water, the base residue containing mostly marine organic matter was combusted as described above and analyzed for radiocarbon at the Leibniz Laboratory AMS facility in Kiel, Germany. The base soluble fraction containing mainly humic acids was acidified until humic acids precipitated, and washed neutral. If sufficient material could be recovered, humic acids were combusted and AMS radiocarbon dated as well.

4.4.2.4 Planktic foraminifera

For each gravity core sample with radiocarbon dated alkenones, a corresponding radiocarbon analysis of foraminiferal shells was performed using sediment subsamples. We chose the planktic species *Globigerina bulloides*, which is the most abundant species in all of the samples. Thus problems in dating resulting from the combined effect of varying abundance and bioturbation [*Broecker et al.*, 1999] should be minimized. From the fraction >150 μm, 10 mg foraminifera shells were hand-picked, cleaned with H_2O_2 following the method described by *Schleicher et al.* [1998] and converted to CO_2 by dissolution in phosphoric acid as described by *Nadeau et al.* [1998]. The gas was purified, reduced to graphite over an iron catalyst in the presence of H_2, and AMS dated at the Leibniz Laboratory facility.

4.4.2.5 Bulk carbonate <40 μm

The sediment fraction <40 μm obtained by wet-sieving was analyzed for carbonate following the methods described above. Accordingly an amount of the sieved sample containing 1 mg carbonate was used for radiocarbon analysis without further treatment using an analogous procedure to that employed for the foraminifera (see above).

4.4.3 Accelerator mass spectrometry dating and data reporting

Quantitative purification of the alkenones and FAMEs yielded between 84 and 344 μg C per sample. Compound specific ^{14}C-AMS analyses were performed using special methods required for the accurate determination of $\Delta^{14}C$ in samples containing <500 - 1000 μg C [*Pearson et al.*, 1998; *von Reden et al.*, 1998]. All other samples contained enough carbon to apply standard methods. To yield fatty acid (FA) ages, the FAME data were corrected to account for the methyl carbon obtained during transesterification. Its contribution was removed by isotopic mass balance [$\Delta^{14}C_{FA} = \{(n+1)*\Delta^{14}C_{FAME}-\Delta^{14}C_{MeOH}\}/n$].

AMS radiocarbon data are reported as defined by *Stuiver and Polach* [1977], using the expressions $\Delta^{14}C$, percent modern carbon (pmC) and conventional radiocarbon ages based on the Libby half-life for fossil samples. For the calculation of sedimentation rates, radiocarbon ages were calibrated to calendar years using the CALIB 4.3 software [*Stuiver and Reimer*, 1993, 2000].

AMS radiocarbon determination in small samples involves a slightly larger uncertainty than standard measurements of large samples [*Pearson*, 2000]. This is due to the relative contribution of the process blank, which is larger in small samples than in large samples. Preliminary work indicates that this blank is ca. 1 μg carbon and has significantly less than modern ^{14}C concentrations [*Pearson et al.*, 1998].

4.5 Results

4.5.1 Bulk parameters, stable oxygen isotopes and $U^{K'}_{37}$

Records of total organic carbon, carbonate, and stable oxygen isotopes of planktic (*G. bulloides*) and benthic (*C. wuellerstorfi*) foraminifera for the two gravity cores are displayed in Figures 4.2 and 4.3. In core G920 the records cover Marine Isotope Stages (MIS) 1, 2 and late stage 3. The glacial period is characterized by high sedimentary contents of TOC (~6-7 %) and relatively low carbonate contents (~50-60%). A drastic increase of carbonate contents and a simultaneous decrease of TOC mark the deglaciation. Relatively uniform carbonate contents of 70 % and TOC contents of 3% prevail during the Holocene. The foraminiferal $\delta^{18}O$ records show the typical glacial/interglacial pattern with an unusually large amplitude of about 3‰ PDB in the planktic record. Estimated SSTs based on $U^{K'}_{37}$ range from about 19°C during the Holocene to approximately 15°C during the glacial period. The transition between the glacial and the Holocene is characterized by several abrupt oscillations. Temperatures are lower during MIS 3 than during the LGM, a feature which is characteristic of alkenone SST records for the study area [*Summerhayes et al.*, 1995; *Kirst et al.*, 1999].

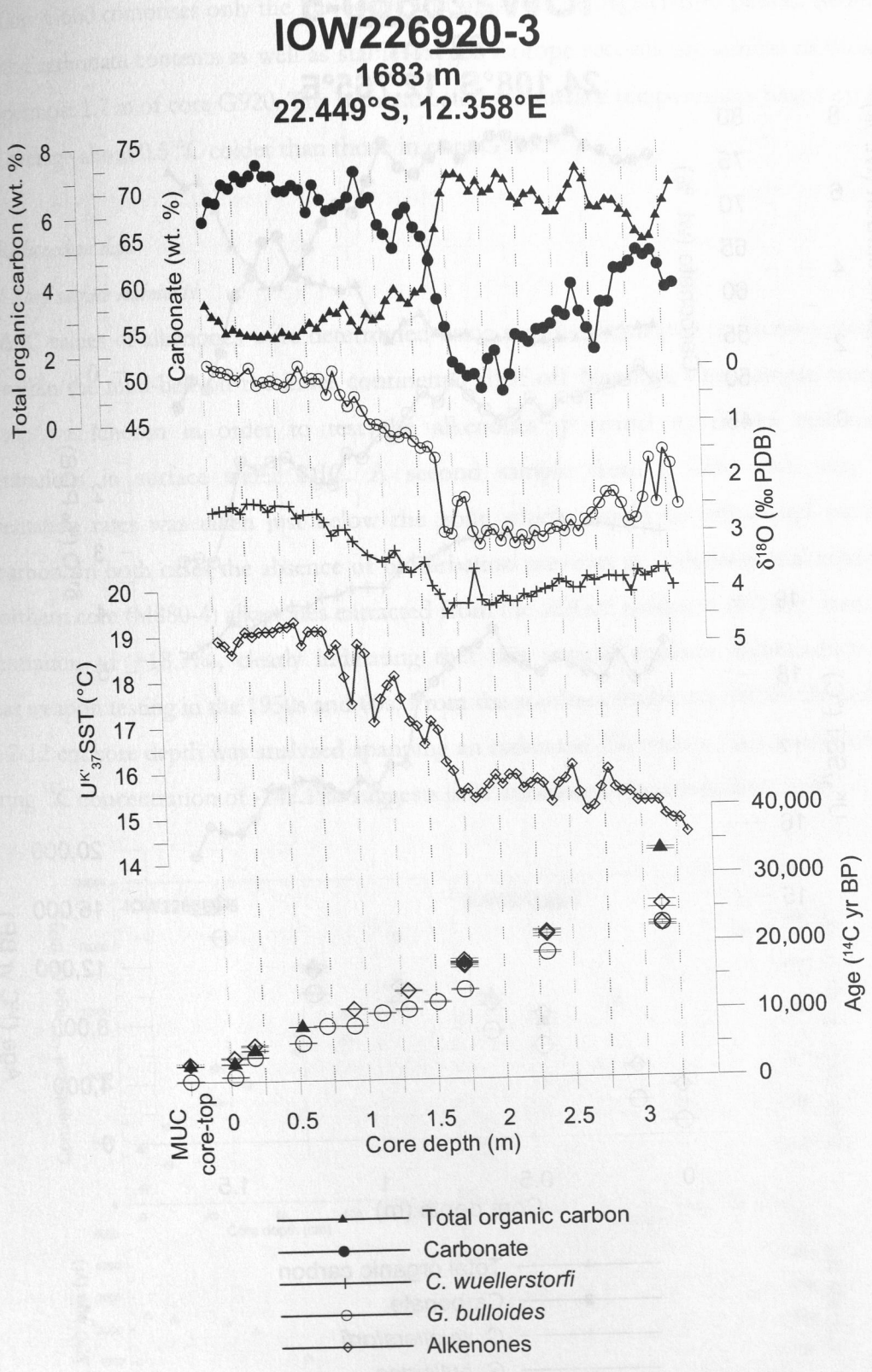

Figure 4.2. Bulk sediment properties, stable oxygen isotope records, $U^{K'}_{37}$ SST estimates and radiocarbon ages for gravity core IOW226920-3 (G920) and the corresponding multicore IOW226920-2 (M920) from the upper continental slope off Namibia.

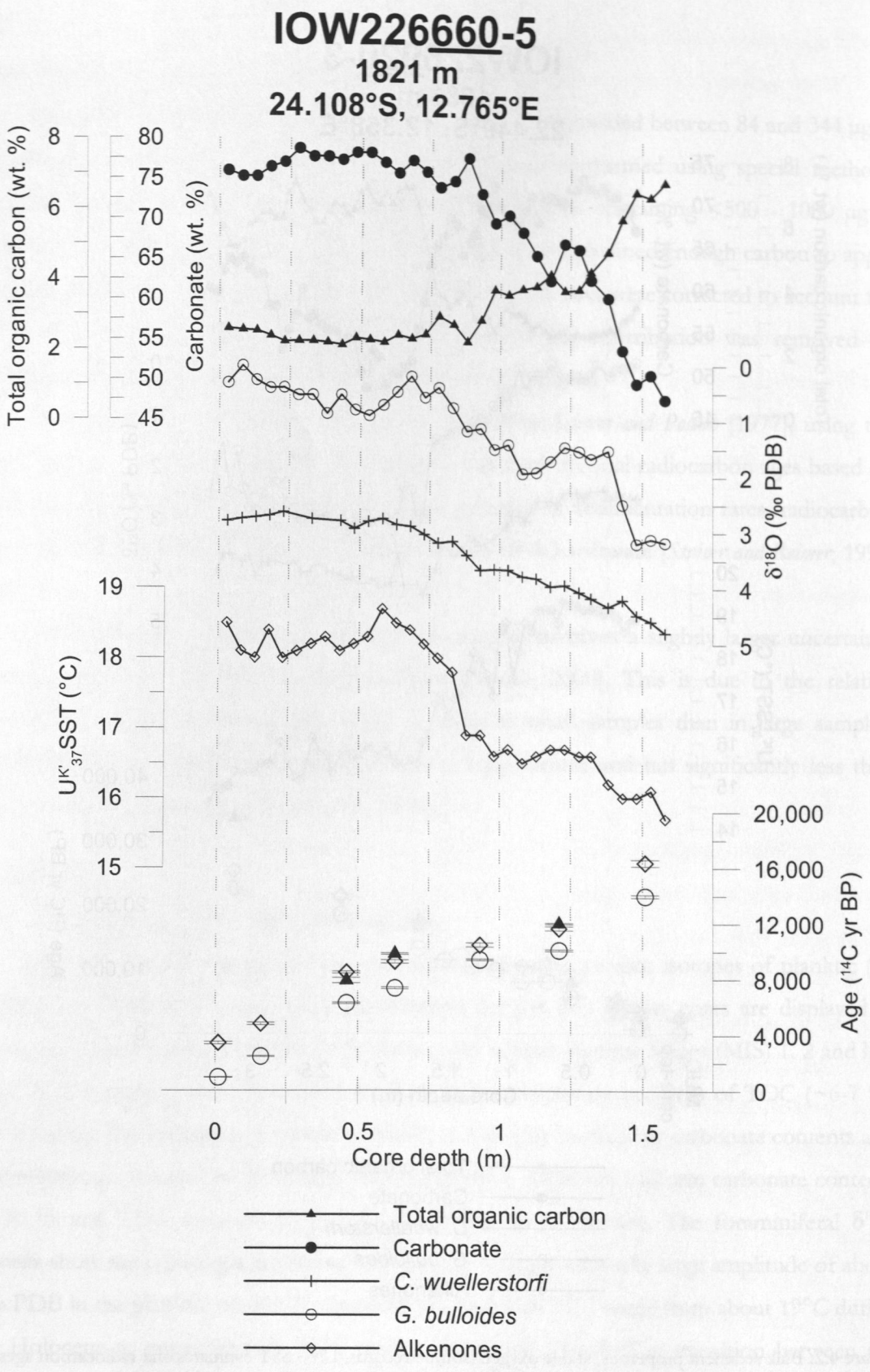

Figure 4.3. Bulk sediment properties, stable oxygen isotope records, $U^{K'}_{37}$ SST estimates and radiocarbon ages for gravity core IOW226660-5 (G660) from the upper continental slope off Namibia.

Core G660 comprises only the Holocene and most of the deglaciation period. Sediment TOC and carbonate contents as well as stable oxygen isotope records are similar to those of the uppermost 1.7 m of core G920. The reconstructed sea surface temperatures based on $U^{K'}_{37}$ are on average about 0.5 °C colder than those in core G920.

4.5.2 Radiocarbon data

4.5.2.1 Shelf surface sediments

$\Delta^{14}C$ values of alkenones were determined using samples from two mulitcores retrieved from within the mud-belt on the inner continental shelf off Namibia. One sample from the core top was chosen in order to test the alkenones' potential to record radiocarbon concentrations in surface water DIC. A second sample from a core with very high sedimentation rates was taken just below the zone which should be influenced by bomb radiocarbon. In both cases the absence of bioturbation prevents post-depositional mixing. In the northern core (M880-4) alkenones extracted from the surface sediment (0-2 cm) have a ^{14}C concentration of +18.7‰, clearly indicating that this sample contains radiocarbon from nuclear weapon testing in the 1950s and 60s. From the southern multicore (M760-2), sediment from 2-12 cm core depth was analyzed spanning an estimated 250 years of accumulation. The resulting ^{14}C concentration of -142.1‰ suggests little influence of bomb radiocarbon.

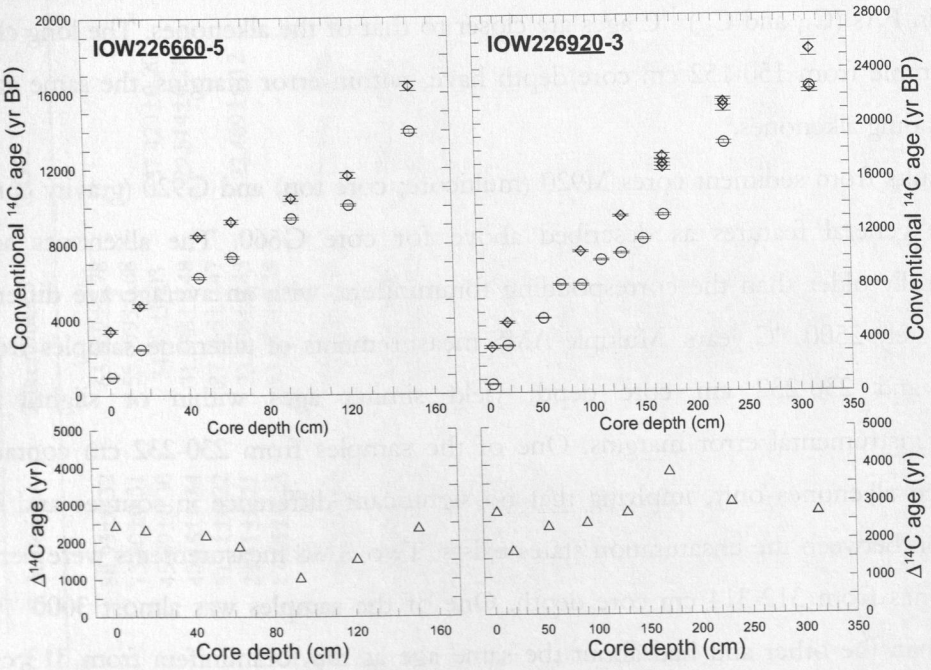

Figure 4.4. Upper two panels: Conventional radiocarbon ages of foraminifera (circles) and alkenones (diamonds) from the two upper slope gravity cores. Error bars depict measuring uncertainty (1σ). Bottom panels: Differences of radiocarbon ages of foraminifera and alkenones.

4.5.2.2 Upper slope sediment cores

AMS results and conventional radiocarbon ages of the different sediment constituents from the upper slope cores are summarized in Tables 4.2 and 4.3 with the major results also displayed in Figures 4.2 and 4.3. Substantial and systematic age differences between foraminifera and alkenones are immediately apparent in data from both cores (Figure 4.4).

In core G660 alkenones are on average 2000 ^{14}C years older than foraminifera from the same sample. Age-depth relationships for foraminifera ages and alkenone ages are almost parallel, and sedimentation rates obtained from linear interpolation between two dated core depths using either one of the age data sets range from around 6-8 cm/kyr during the Holocene to up to 18 cm/kyr during the deglaciation. Age differences between bulk TOC and foraminifera are on the same order of magnitude as the differences between alkenones and foraminifera. Age differences between TOC and alkenones are relatively small and not always in the same sense, with TOC being up to 600 ^{14}C years younger or older than the alkenones. A trend from negative to positive TOC-alkenone age differences with increasing core depth is evident. Ages of organic residues from base treatment are 700-2400 ^{14}C years older than TOC. Their ages are identical to those of the alkenones (45-47 cm) or 1305 to 2730 ^{14}C years older. Humic acids in the sample from 45-47 cm core depth are ~900 ^{14}C years younger than the corresponding alkenones and have an age more similar to TOC. The C_{16} fatty acid (FA) in the core top sample (0-2 cm) is only 180 ^{14}C years older than the foraminifera while corresponding long-chain FAs (C_{24} and C_{26}) ^{14}C ages are closer to that of the alkenones. The long chain FAs of the sample from 150-152 cm core depth have, within error margins, the same age as the corresponding alkenones.

Results from sediment cores M920 (multicore; core top) and G920 (gravity core) show the same general features as described above for core G660. The alkenones are again systematically older than the corresponding foraminifera, with an average age difference of approximately 2500 ^{14}C years. Multiple AMS measurements of alkenone samples from 170-172 cm and 230-232 cm core depth yield similar ages within or slightly outside analytical/instrumental error margins. One of the samples from 230-232 cm contained di-unsaturated alkenones only, implying that no significant difference in sources and isotopic distribution between the unsaturation states exists. Two AMS measurements were performed on alkenones from 312-314 cm core depth. One of the samples was almost 3000 ^{14}C years younger than the other and had about the same age as the foraminifera from 313 cm core depth. The younger age, however, is probably the result of contamination, since combustion of the sample yielded significantly more carbon than what was expected from GC analysis of the sample. Foraminiferal ages of the samples from 71 cm and 91 cm core depth are identical

Table 4.2. AMS results of samples from the upper continental slope reported as percent modern carbon (pMC); FAME is short for fatty acid methyl ester.

	pMC [%]							
Depth in core (cm)	***G. bulloides***	**Alkenones**	**TOC**	**Base residue[a]**	**Humic acids[b]**	**C_{16} FAME[c]**	**C_{24}/C_{26} FAME[c]**	**Carbonate <40μm**
Core IOW226660-5						82.44±0.76	68.8±0.47	
0-2 (1)[d]	88.93±0.32	65.369±0.78						
15-17 (16)	73.80±0.31	55.099±0.68						
45-47 (46)	45.89±0.30	34.89±0.03	37.429±0.20	34.42±0.22	38.36±0.28			
62-64 (63)	40.15±0.34	31.688±0.48	29.514±0.20	26.95±0.15				
92-94 (93)	31.11±0.22	27.265±0.47						
120-122 (121)	28.51±0.21	23.398±0.43	22.469±0.12	16.70±0.16			12.36±0.23	
150-152 (151)	17.58±0.24	13.073±0.38						
Core IOW226920-2						91.8±0.92	86.28±1.06[e]	
0-1	99.70±0.46	73.259±1.24	75.351±0.36	71.26±0.27				72.79±0.38
Core IOW226920-3								
2-4 (3)	92.46±0.41[f]	86.34±0.57	72.84±0.32					
17-19 (18)	64.64±0.29	52.178±0.55	57.21±0.35	54.83±0.35				
52-54 (53)	50.18±0.29		37.239±0.18	33.37±0.18	38.74±0.20			36.64±0.21
70-74 (71)	36.85±0.27							
90-92 (91)	36.90±0.29	27.101±0.22						29.83±0.20
110-112 (111)	29.32±0.20							
129-131 (130)	27.62±0.22	19.634±0.17						23.90±0.18
150-152 (151)	24.24±0.21							
170-172 A[g]		12.502±0.44						
170-172B1[g] (171)	19.43±0.19	11.328±0.27	11.927±0.09	11.32±0.10		20.96±0.27	12.75±0.21	
170-172 B2[g]		12.033±0.34						
230-232 (231)	10.02±0.17	6.838±0.25						
230-232		7.104±0.39[h]						
312-314 B[i] (313)	5.98±0.16	4.252±0.03	1.552±0.04	1.49±0.07				
312-314 A[i]		6.048±0.26						

[a] acid treated organic matter insoluble in NaOH
[b] organic matter soluble in NaOH
[c] FAME pMC are not corrected for contribution of methyl carbon obtained from methanol ($\Delta^{14}C$=-995.6) during transesterification
[d] depth in parentheses refer to carbonate samples (foraminifera and fine-fraction carbonates)
[e] C_{26} FAME only
[f] mixed sample of planktic species *G. bulloides* and *O. universa*
[g] sample 170-172 was separated into A and B after urea adduction; split B was further divided in two parts after combustion to CO_2
[h] di-unsaturated alkenones only
[i] Sample 310-312 was separated into A and B splits after urea adduction

Table 4.3. Conventional radiocarbon ages of samples from the upper continental slope calculated from the data in table 4.2, using the Libby-halflife [*Stuiver and Polach*, 1977].

Depth in core (cm)	Conventional radiocarbon age, ^{14}C years BP							
	G. bulloides	Alkenones	TOC	Base residue[a]	Humic acids[b]	C_{16} fatty adics[c]	C_{24}/C_{26} fatty acids[c]	Carbonate <40μm
Core IOW226660-5								
0-2 (1)[d]	940±30	3410±95				1120±75	2730±55	
15-17 (16)	2440±35	4790±100						
45-47 (46)	6255+55/-50	8460±70	7890±200	8470±50	7595+60/-55			
62-64 (63)	7330±70	9230±120	9800±55	10535±45				
92-94 (93)	9380+60/-55	10450±140						
120-122 (121)	10080±60	11650±150	12000±45	14380±80				
150-152 (151)	13960±110	16350±240					16540±150	
Core IOW226920-2								
0-1	25±35	2500±140	2270±40	2720±30		250±80	930±100[e]	
Core IOW226920-3								
2-4 (3)	630±35[f]	3410±100	2550±25					2550±40
17-19 (18)	3505±35	5230±85	4490±50	4830±50				
52-54 (53)	5540±45		7930±50	8815±45	7620±40			
70-74 (71)	8020±60							8065±45
90-92 (91)	8010±60	10500±65						
110-112 (111)	9855±55							9715±55
129-131 (130)	10340±60	13100±70						
150-152 (151)	11380±70							11500±60
170-172 A[g]		16700±280						
170-172B1[g] (171)	13160±80	17000±230	17100±65	17500±70		12070±100	16290±130	
170-172 B2[g]		17500±190						
230-232 (231)	18480±130	21500±290						
230-232		21200±440[h]						
310-312 B[i] (311)	22630±210	25400±570	33500±200	33810 +370/-360				
310-312 A[i]		22500±340						

[a] acid treated organic matter insoluble in NaOH
[b] organic matter soluble in NaOH
[c] measured FA ages are corrected for contribution of methyl carbon obtained from methanol ($\Delta^{14}C$=-995.6) during transesterification by isotopic mass balance
[d] depth in parentheses refer to carbonate samples (foraminifera and fine-fraction carbonates)
[e] C_{26} FA only
[f] mixed sample of planktic species *G. bulloides* and *O. universa*
[g] sample 170-172 was separated into A and B after urea adduction; split B was further divided in two parts after combustion to CO_2
[h] di-unsaturated alkenones only
[i] Sample 310-312 was separated into A and B splits after urea adduction

within error margins. Except for this depth, ages increase with core depth, and sedimentation rates obtained from linear interpolation of foraminifera or alkenone ages yield similar values (5-8 cm/kyr during the Holocene, 10-20 cm/kyr during the deglacial and the LGM). TOC and base residues have similar ages as the alkenones from the same samples with differences less than 900 ^{14}C years, except the sample from 312-314 cm, where TOC and the base residue are approximately 8000 ^{14}C years older than the alkenones and about 11000 years older than the foraminifera.

In the core top (0-1 cm) sample from the multicore M920, foraminifera and C_{16} FAs have recent to sub-recent radiocarbon ages. The C_{26} FA is older than the short-chain ones (age difference = 680 ^{14}C years), but significantly younger than the alkenones (age difference = 1570 ^{14}C years). In the sample from 170-172 cm of the gravity core G920, in contrast, long-chain FAs are younger than alkenones (age difference = 710 ^{14}C years) and about 3000 ^{14}C years older than the foraminifera from that core depth, while the C_{16} FA age is even younger than the foraminifera age. Fine-grained (<40 μm) carbonates are older than the co-occurring foraminifera in the sample from 3 cm core depth with a radiocarbon age identical to TOC. In the samples of early Holocene and deglacial age from deeper in the core, the age of fine-grained carbonates is almost indistinguishable from that of the foraminifera.

4.6 Discussion

In order to explain the large age differences between foraminifera and co-occurring alkenones several aspects have to be considered. Confidence in the reliability of alkenones as tracers for radiocarbon concentration of the ambient dissolved inorganic carbon (DIC) is an important prerequisite for the interpretation of the records. Secondly, upwelling systems are highly dynamic, and temporally variable surface water conditions combined with seasonality of plankton growth may cause different tracers to record different environmental conditions. Finally, sedimentation processes and their potential influence at the study sites must be assessed.

4.6.1 Marine biomarkers as tracers for surface water radiocarbon

Molecular markers of primary producers should, by definition, be effective tracers of surface ocean (euphotic zone) conditions, and their ability to record $\Delta^{14}C$ of surface water DIC has been demonstrated in sediments from the Santa Monica and Santa Barbara Basins [*Pearson et al.*, 2000]. Phytoplankton derived sterols isolated from undisturbed sediments spanning a pre-bomb/post-bomb transition yielded the same $\Delta^{14}C$ values as foraminifera

from the same sediments, both values closely tracking the evolution in surface water DIC $\Delta^{14}C$ [*Pearson et al.*, 2000]. Alkenones from core top sediments from the Santa Barbara Basin and from the Gulf of Mexico contain radiocarbon from nuclear testing (N. Ohkouchi, WHOI, unpublished results), indicating that this group of marine biomarkers is likewise capable of recording surface water DIC. The post-bomb alkenone age of one surface sediment sample from the Namibian shelf confirms these findings. The second shelf sample from 2-12 cm core depth of multicore 760 was AMS dated to be 1180 ^{14}C years old. This sample was taken below the uppermost core section in order to avoid influence of bomb-radiocarbon. Assuming no benthic mixing owing to suboxic bottom water conditions at this site [*Weeks et al.*, 2002], this shelf sample should not contain any bomb radiocarbon, even if sedimentation rates of up to 40 cm/kyr are assumed. Published sedimentation rates from the inner Namibian shelf are variable and attain values up to ~170 cm/kyr [*Vetrov et al.*, 1996; *Struck et al.*, in press], but these data were determined from cores taken in the central part of the "mud belt", whereas our core is from near its margin.

The natural $\Delta^{14}C$ of DIC in upwelled water on the Namibian shelf prior to nuclear weapon testing is unknown and may be substantially lower than the average marine surface water value of ~-50 ‰, equivalent to a reservoir age of 400 years. Reservoir ages in upwelling regions may approach as much as 1300 years ($\Delta^{14}C$=-150‰) [*Stuiver et al.*, 1986; *Southon et al.*, 1990]. If a uniform sedimentation rate of 40 cm kyr^{-1} is assumed, the sample should have an approximate reservoir corrected "true" age of 175 years representing the average age between 12 cm (12 cm/40 cm kyr^{-1}= 300 yr) and 2 cm (2 cm/40 cm kyr^{-1} = 50 yr). Since the measured age is hence consistent with a natural reservoir age of ~1000 years we conclude the alkenones in sample 2-12 cm to realistically record surface water DIC.

4.6.2 Radiocarbon data from the upper continental slope

Planktic foraminifera from the core top of multicore M920 from the upper continental slope exhibit a radiocarbon age of 25 ^{14}C years. The natural reservoir age of surface waters is at least 400 years, in the Benguela upwelling area probably up to 1000 years, as discussed above. This indicates that the AMS dated foraminifera at this site contain radiocarbon from nuclear weapon testing, reaffirming the recent sedimentation. In contrast, alkenones from this core top sample are 2500 ^{14}C years old. Down-core records of both gravity cores display similar age offsets between foraminifera and alkenones and foraminifera and TOC, with the organic material being always older, implying that a systematic process causes these offsets.

4.6.2.1 Upper slope sediment stable oxygen and $U^{K'}_{37}$ records

Stable oxygen isotope records of *Globigerina bulloides* in gravity core G920 have a large glacial to interglacial amplitude, implying a large and relatively abrupt temperature change from the LGM to the Holocene (Figures 4.2 and 4.3). Alkenones, in contrast, suggest a gradual warming from coolest temperatures during MIS 3 to warm SSTs during the Holocene. An obvious question therefore is, whether these differences could be caused by the same mechanism as the age offsets.

G. bulloides is a species that thrives preferentially, but not exclusively, in upwelling waters [e.g. *Bé*, 1977]. Highest fluxes of *G. bulloides* presently occur in response to upwelling events in the Benguela area, whereas fluxes of alkenone producers show no temporal relation to upwelling events and are higher in the season with weaker upwelling [*Giraudeau et al.*, 2000]. Under low sea-level conditions during the glacials, *G. bulloides* living within upwelling cells near the core sites would record lowest sea surface temperatures and lowest $\Delta^{14}C$ in the freshly upwelled waters containing "old" DIC. Alkenone temperatures in contrast would represent closer to annual average values including the warmer SSTs prevailing between upwelling events, and alkenone producers would probably incorporate DIC richer in ^{14}C. When a critical sea-level was reached during deglaciation, the upwelling cell may have shifted to a near-shore position similar to the modern situation. This scenario could explain why stable oxygen isotopes of planktic foraminifera imply a large and abrupt temperature shift, whereas reconstructed sea-surface temperature records based on alkenones show a smaller shift and a gradual change. However, this would also imply much smaller (<1kyr) than observed age differences due to incorporation of DIC with different radiocarbon concentrations. Moreover, an age difference related to such a process would be in the opposite direction than observed, i.e. foraminifera would appear older than alkenones.

Instead, the age difference measured between alkenones and foraminifera must be a secondary signal resulting from processes which occur between production and final burial in the sediment. These processes may, in turn, have aliased the corresponding proxy records.

4.6.2.2 Bioturbation

^{14}C age offsets between coarse-grained and fine-grained carbonates [*Paull et al.*, 1991; *Thomson et al.*, 1995, *Brown et al.*, 2000] have been reported, but in most cases, fine-grained particles were significantly younger than coarse-grained particles. Differential bioturbational mixing has been suggested as a possible mechanism to explain such offsets,

requiring homogeneous mixing in a surface layer, which is thinner for coarse-grained particles than for fine-grained particles. The age differences observed in the samples from the Namibian continental slope are in the opposite sense, given that organic matter (and, by inference, the alkenones) is concentrated in the fine fraction [*Keil et al.*, 1994; *Sachs et al.*, 2000]. In order to explain older fine fraction ages by bioturbation, a preferential upward transport of fine-grained and organic rich particles over relatively long distances would be required. This would mean that the bioturbation process is dominated by organisms that transport sediment from some depth within the sediment to the sediment surface. Detailed investigation of the distribution of radionuclides as tracers for bioturbation carried out at various deep-sea sites, however, revealed that transport processes from the surface to depth within the sediment are more common [e.g. *Wheatcroft* 1992; *Wheatcroft et al.*, 1994; *Thomson et al.*, 2000]. Moreover, high sedimentation rates and low oxygen conditions which prevail on the Namibian continental slope should suppress the effects of bioturbation [*Anderson*, 2001; *Bard*, 2001]. Therefore we consider bioturbation a minor factor in producing the age offsets between foraminifera and alkenones.

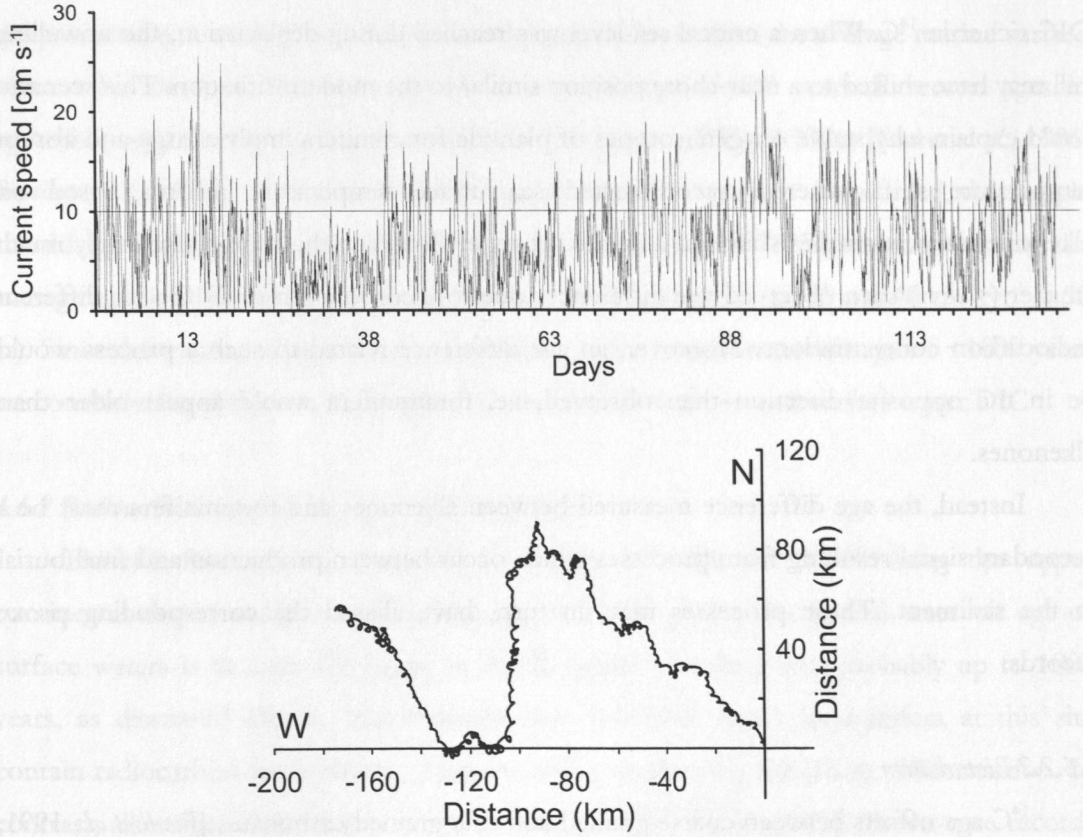

Figure 4.5. Data recorded by a current meter moored at 22.004°S, 12.390°E at 1100 m water depth 5 m off the sea-floor (G. Nelson, University of Cape Town, unpublished data). Current velocities (top); current speeds above horizontal line are sufficient for resuspension of organic aggregates according to Lampitt (1995) and Thomsen and Gust (2000). Lower panel: Progressive vector over entire mooring period of 133 days, indicating net sea-ward transport

4.6.2.3 Lateral advection

Alkenones and TOC older than foraminifera could be explained as the result of admixture of laterally advected, older organic material. Based on their recent depositional age in the core top of M920, foraminifera on the upper continental slope may be assumed to be autochthonous. Fine-grained organic matter, including alkenones, may be advected from elsewhere. The inner continental shelf with sediments rich in organic matter is a possible source. Alkenones in these shelf sediments are probably autochthonous since the distribution of organic matter in surface sediments correlates with productivity patterns in the overlying waters [*Mollenhauer et al.*, in press; Chapter 3], and the presence of bomb radiocarbon in these compounds from the core top at the northern site 880 suggests rapid deposition at or near the site of production. Lateral transport of particulate matter is largely driven by the hydrodynamics within the benthic boundary layer (BBL), which controls the particle exchange between sea-floor sediments and the water column [*Dickson and McCave*, 1986; *McCave*, 1986; *Thorpe and White*, 1988].

In order to produce age offsets of several thousand years between foraminifera and alkenones and between foraminifera and TOC, a long residence time of alkenones and of bulk TOC in the benthic boundary layer would be required. Owing to their relatively low reactivity and slow degradation [*Grimalt et al.*, 2000 and references therein], alkenones could survive within the BBL, particularly when they are firmly adsorbed to or protected by inorganic particles such as clays [*Hedges et al.*, 2001]. Alkenones associated with inorganic particles protecting them from degradation could then be transported over long distances, whereas autochthonous alkenones would be degraded rapidly. As a result of continuous resuspension and the low settling velocities of organic matter in fluffy aggregates, the material could reside in the BBL for a long time, while being laterally transported according to the flow conditions. *Thomsen and Gust* [2000] experimentally determined that bottom flow velocities of 9-23 cm s^{-1} at 1 m above the sea-floor represent a critical threshold velocity for resuspension of the top-layer organic aggregates in the 140-450 μm size range. This confirms previous findings that particles from an algal bloom are re-suspended at current velocities >10 cm s^{-1} [*Lampitt*, 1985].

Upwelling systems are often characterized by strong bottom currents. The outer shelf off Namibia is poor in organic matter and is probably strongly influenced by current winnowing [*Mollenhauer et al.*, in press; Chapter 3], whereas on the inner shelf, deposition of soft, fine-grained sediment occurs in troughs protected from current winnowing. Bottom current influence is also evident from the sediment distribution on the upper slope [*Mollenhauer et al.*, in press; Chapter 3]. A current meter moored at 1100 m water depth

(22.004 °S, 12.39 °E) and 5 m above the sea-floor recorded strong semidiurnal tides with velocities episodically as high as 15-25 cm s^{-1} and a net seaward transport (Figure 4.5; G. Nelson, Univ. of Cape Town, unpublished data). This tidal water movement is much more vigorous than the general poleward drift, which is reported from the outer shelf and upper slope and has velocities of around 1.8 cm s^{-1}. These bottom water flow conditions on the upper continental slope off Namibia will lead to continuous re-suspension and net seaward transport of top-layer organic aggregates. These particles could eventually be deposited at the core sites in water depths of 1600 to 1800 m, after an average residence time within deposition/re-suspension loops of approximately 2500 years.

The age distribution of FAs, TOC, base insoluble organic matter and humic acids is consistent with a scenario in which lateral advection is the principal factor controlling the age relationships between sedimentary components. The reactivity of individual compounds will determine their average residence times in the BBL, as the probability to survive for a long time in the BBL increases with increasing resistivity to degradation. In other words, labile compounds survive only when they are rapidly sequestered in the sediment. Short chain fatty acids are less resistant to degradation than long chain fatty acids [*Canuel and Martens*, 1996] and alkenones [*Volkman et al.*, 1980]. Therefore, the short-chain fatty acids would be expected to have a shorter average residence time in the BBL than the latter, which is indicated by their age being indistinguishable from that of foraminifera in core top sediments and closer to foraminifera than to long-chain fatty acids at 170-172 cm. The age of long chain fatty acids is between the ages of short chain fatty acids and alkenones in the core top sediments, yet it is similar to that of the alkenones at 170-172 cm (~17000 ^{14}C years BP). The general pattern of age distribution between the different biomarkers is hence consistent with what would be expected from the respective degradation rates. The significance of this observation, however, can only be assessed with more molecular isotopic measurements conducted at finer depth resolution and over a broader suite of organic compounds.

Base insoluble organic matter is always slightly older than TOC and humic acids. The former fraction is likely to contain the most refractory material, as by treatment with sodium hydroxide, humic material derived from hydrolysis of labile marine biopolymeric materials is removed. Variable but small age differences between TOC, humic acids and base insoluble organic matter indicate that the composition of TOC is not constant over time. It can be speculated that the old TOC and base insoluble organic matter in the lowermost sample from G920 may be the result of admixture of fossil organic matter (e.g., via oil seepage).

Fine fraction carbonates of a sample from near the core top are slightly younger than alkenones and TOC, but significantly older than foraminifera from the same sample. This may indicate that lateral advection of fine-grained particles on the upper slope beneath the Benguela upwelling system affects carbonates as well as organic matter. Coccoliths deriving from the same phytoplankton group as the alkenones are small and should reside in the <40 μm size fraction [cf. *Paull et al.*, 1991], whereas unfragmented foraminifera shells are sand-sized. That fine-grained carbonates are coeval with foraminifera in the samples from deeper core depths may be the result of carbonate dissolution in organic rich sediments [*Wenzhöfer et al.*, 2001] and/or subsequent fragmentation of foraminifera tests [e.g. *DuBois and Prell*, 1988], thus increasing the relative contribution of foraminiferal calcite to the <40μm size fraction. Another factor that may influence the age of fine-grained carbonates is the carbonate concentration of advected material, which may change over time depending on conditions in the source area. If carbonate is abundant in the source area, the relative contribution of advected material to the fine-grained carbonate fraction would be high and its radiocarbon age would be old. If low carbonate concentrations prevail in the source area, little carbonate could be advected to the study sites, which would result in younger ages of the calcareous fine fraction.

With the methods available, it is not possible to identify precisely the source area of the advected organic material. However, considering the $U^{K'}_{37}$-based estimate of modern sea-surface temperatures in the core tops of the two cores, which are about 1 °C higher than the annual average sea surface temperature [*Levitus and Boyer*, 1994], a source area slightly north of the respective core sites is suggested. The average difference between the SST estimates for the two cores is ~0.5°C, which is within the range of what would be expected because of the ambient SST difference at their respective geographic positions. A northern source would be consistent with transport by the general poleward drift on the shelf, but trajectories of the tidal movement point in the opposite direction. Another possibility is that the temperature reconstructed from the $U^{K'}_{37}$ may contain a bias toward warmer conditions due to the seasonal cycle of alkenone producers and their occurrence in-between rather than during upwelling events [cf. *Giraudeau et al.*, 2000].

Net export of organic matter from the shelf to the slope and concomitant aging of organic matter as suggested above is consistent with the observations at other continental margin sites. Surface sediment TOC ages of approximately 3500 years were reported for the NW European margin [*Hall and McCave*, 1998] and old suspended particulate organic matter was found on the continental margin of Eastern North America [*Bauer et al.*, 2001]. Further evidence is provided by increased material fluxes in deep relative to ow

sediment traps observed on the European continental slope [*Lampitt et al.*, 1995], on the NW African continental margin [*Freudenthal et al.*, 2001] and in the Norwegian and Barents Seas [*Thomsen et al.*, 1998]. At the latter two sites, discrepancies between $U^{K'}_{37}$ based temperature estimates and local SSTs were observed associated with increased fluxes of material, further implying the advection of allochthonous particles to the traps. However, discrepancies between $U^{K'}_{37}$ data and local temperatures only provide circumstantial evidence for advective control on this proxy; alternatively such discrepancies could be caused by local problems with the calibration of the $U^{K'}_{37}$ index. Similarly, old TOC ages, especially on continental margins, could be influenced by relict terrigenous OC. In contrast, direct measurements of ^{14}C of alkenones relative to microfossils unequivocally prove an older age of the biomarkers.

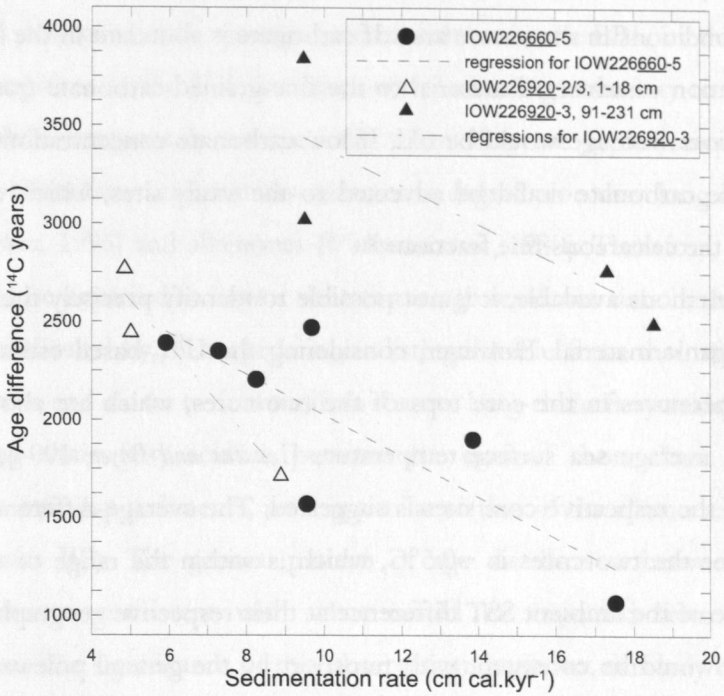

Figure 4.6. Sedimentation rates versus radiocarbon age difference between foraminifera and alkenones. Linear fits are indicated by dashed lines.

4.6.2.4 Down-core variations in age offsets

Age offsets between foraminifera and alkenones are similar in all samples, but not constant. Instead, variations occur that could be related to changes in the sedimentary environment. However, a quantitative treatment of the data by expression of the results as ^{14}C abundance in each component at the time of deposition as has been done by *Ohkouchi et al.* [submitted] is not feasible in the Bengeula system. The reason is that such a calculation would be based on a reliable absolute age model, the determination of which would require

knowledge of the reservoir correction to be applied. As discussed above, the precise reservoir age of surface waters in the Benguela system is unknown. It is probably larger than ocean average and may vary in response to variable upwelling rates. In this study, we discuss the temporal evolution of age offsets between foraminifera and alkenones semi-quantitatively.

Age differences between foraminifera and alkenones could vary with bulk sedimentation rate. To test this, sedimentation rates based on linear interpolation of foraminiferal radiocarbon ages calibrated to calendar years were calculated. The foraminifera are interpreted to be autochthonous based on their younger age. For each individual core depth, the sedimentation rate was calculated between the two adjacent dated core depths. For the uppermost and the lowermost sample from each core, sedimentation rates were calculated by linear interpolation to the nearest dated core depth. The sedimentation rates calculated by this method, however, are only an approximation, as they are determined assuming that the sediment accumulates at constant rates over time. They represent average values over time rather than the particular rate at a certain point in time and are thus subject to uncertainty.

A significant negative correlation (r^2=0.67; n=7) exists between sedimentation rate and age difference in core G660 (Figure 4.6), i.e. age differences are smaller at higher sedimentation rates. This implies that the average residence time of organic aggregates in the BBL is reduced when sediment is accumulating at high rates. The time organic particles remain at the sediment-water interface, where they can episodically be suspended by currents, is shorter at higher sediment accumulation rates. For core G920 such a relationship between sedimentation rate and age difference does not exist if all data are considered. However, distinct trends are apparent when the uppermost core section (1-18 cm) (r^2=0.93; n=3) and the glacial to deglacial core section (91-231 cm) (r^2=0.66; n=4) are considered separately (Figure 4.6). The relationships in these two sections differ in the slope. More importantly, in the glacial to deglacial core section, age differences are higher at sedimentation rates that approximate those calculated for the late Holocene. A possible interpretation of this is that changes in current regimes could play a role in determining the average residence time in the BBL. Current velocities and trajectories could change in response to sea-level variations and other hydrographic conditions.

Variable trends in the age difference versus sedimentation rate relationships might arise, when allochthonous material is transported from source areas at variable distances from the site of deposition and accordingly remains in sedimentation/re-suspension loops. If stronger bottom currents prevailed over longer distances, advected material may be older

at the time of deposition than when it is transported over shorter distances. The relative contribution of allochthonous material with different depositional ages may also influence the slopes of the trends.

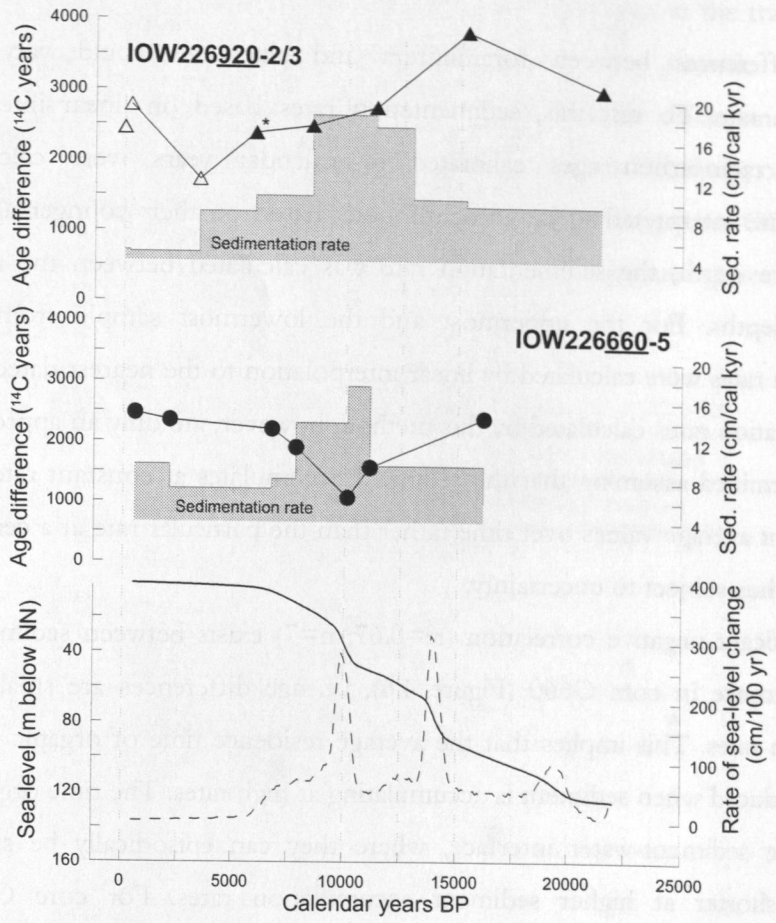

Figure 4.7. Radiocarbon age difference between alkenones and foraminifera, and sedimentation rates over the last 25,000 calendar years for core G920 (upper panel), G660, middle panel. Global sea-level and rate of sea-level change according to *Fleming et al.* [1998] (lower panel). Asterisk in upper panel marks core depth 52-54, where the age difference is taken between TOC and foraminifera instead of between alkenones and foraminifera.

When discussing temporal changes in hydrographic conditions, other factors such as changes in sediment input and source areas of the laterally advected material must be considered. In particular, during the glacial, when the inner shelf was exposed, and during the rapid sea-level rise at the deglaciation, when the shelf was flooded again, older material originally deposited on the shelf may have been eroded and probably contributed to the sedimentation at the study sites on the upper slope. The relationship between sea-level and sedimentation rate is indicated by increased sedimentation rates occurring at times of rapid sea-level rise at core-site G920 (Figure 4.7). Erosion of older shelf material may thus explain why age differences are larger in the older sections of core G920. The largest age

difference between foraminifera and alkenones occurs just after the sea-level started to ris according to *Fairbanks et al.* [1992] or *Fleming et al.* [1998]. This provides evidence that these times input of eroded shelf material as described above played an important role. A the southern site G660 the temporal development of age differences suggests that this sit was probably influenced by sea-level change in a different way. Here, sedimentation rate increased significantly at around 10 calendar kyr BP, which may be related to the secon phase of rapid sea-level rise seen in the sea-level curves [*Fairbanks et al.*, 1992; *Fleming et a* 1998]. This scenario, however, would require that the allochthonous material that wa deposited at site G660 at that time did not contain large amounts of older alkenones. It not possible to reconstruct what type of material was eroded from the shelf and where derived from. Modern sediments on the Benguela shelf are strongly heterogeneous, whic implies that fossil deposits may likewise have been formed in different facies and hav contained different amounts of organic material.

Changing source area and varying contribution of older alkenones with largest inpu of allochthonous material during the deglaciation may in part also explain why a gradu increase in SST is reconstructed based on $U^{K'}_{37}$, whereas from planktic foraminiferal stabl isotope records, colder glacial temperatures with an abrupt increase at the deglaciation ar derived.

4.7 Conclusions

Large age offsets between foraminifera and alkenones observed in sediment core from the upper continental slope off Namibia are considered to be the result of sedimen redistribution processes. Organic matter associated with the fine fraction is resuspende and advected laterally by bottom currents. Whereas the source area of the particles probably proximal to the core sites, repeated sedimentation/re-suspension cycles result i >1 kyr temporal offsets between the molecular and microfossil records. The inner shel where organic matter is abundant and apparently autochthonous, is one possible source fo this advected material.

As a significant fraction of the organic matter at the core sites is allochthonou paleoceanographic proxy information derived from molecular markers must be treate with caution. Whereas general regional trends are probably captured, local effects are no faithfully recorded, as the material is probably composed of a mixture of material fro different sources. The different age scale for the organic matter has to be considered whe comparing organic proxy records with data derived from foraminifera, and apparen

temporal leads or lags between such records from upper continental margin sediments may be secondary signals.

Age offsets are likely caused by the site specific current regime and other local factors affecting the sedimentation processes. They vary from site to site, illustrating the heterogeneous depositional pattern in the Benguela upwelling area. However, this also means that the age offsets between foraminifera and alkenones are a local effect, which would not be expected at sites of lower bottom water current energy. It is not obvious why age differences between foraminifera and alkenones only vary slightly over time, even though the oceanographic conditions have changed substantially over the same time period. A speculative theory would be that the average age difference observed at a certain site is dependent upon the general current regime. Currents controlling the build-up of drift deposits such as the Bermuda Rise are more vigorous and act over much longer distances than the currents occurring on the Benguela continental slope, which are a rather local phenomenon. Consequently, age offsets measured at the Bermuda Rise are much larger and more variable [*Ohkouchi et al.*, subm.] than those observed in this study. Further research at sites with different oceanographic conditions is necessary to better understand the underlying sedimentary processes.

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Conclusions and perspectives

In this thesis, the distribution and amount of organic carbon accumulation in the South Atlantic Ocean for modern, mid-Holocene and last glacial time slices were investigated. A detailed study in the Benguela upwelling area was carried out in order to assess small scale processes and the relative importance of high productivity systems. Sedimentation processes affecting the organic fraction were analysed and first estimates of temporal offsets between production and burial of organic matter were made.

Most of the organic matter in marine sediments is found along the continental margins, while in comparison accumulation in the pelagic realm is relatively small. Total amounts of annual accumulation in pelagic sediments at water depths >3000 m are on the order of $1.8 * 10^{12}$ g C. At least a similar amount of organic carbon accumulates as in the pelagic area along the continental margins. For example in the Benguela upwelling system which is the most productive area of the South Atlantic, annual accumulation of organic carbon is approximately $2.5 * 10^{12}$ g C. The budgets calculated within this thesis indicate that the amounts of carbon removed from the active reservoirs via burial are small compared to for instance annual anthropogenic CO_2 emissions. Terrestrial input was ignored for this estimate because insignificant relative contributions are expected in the pelagic realm. The same holds true for the Benguela upwelling area, which is a highly productive marine environment and located adjacent to a desert with little vegetation on land. Thus input of organic matter from terrestrial sources is regarded to be insignificant.

The estimates of modern accumulation of organic carbon are based on surface sediment data which are still subject to diagenetic alteration. Much of the organic matter deposited in the sediments may eventually be decomposed, releasing CO_2 into the deep water. The relative amount of organic carbon lost from the sediments by these processes is unknown, as are the timescales over which these diagenetic processes will be active. Possibly, even LGM sediments are still subject to diagenetic breakdown, and organic matter may still be degrading. Benthic flux rates and quantification of these fluxes thus an important field for further investigations.

Mid-Holocene and LGM organic carbon accumulation in the Benguela high production system do not vary significantly. Higher accumulation rates during the LGM with respect to Holocene values observed at sites on the continental slope are probably to great extent due to the effects of lower glacial sea-level, which results in a lateral displacement of upwelling centres. A glacial reduction of the depositional area on the continental shelf due to sea-level lowstand combined with possibly increased accumulation in the remaining depositional area results in more or less equal amounts of

accumulation in the area during the LGM and the Holocene. Comparison of mid-Holocene and LGM organic carbon accumulation in the pelagic realm (>3000 m water depth) shows that glacial increases are approximately 2 to 3 fold. However, the total amount accumulating in the pelagic ocean is small compared with the amounts accumulating along continental margins. Hence, doubling of pelagic accumulation rates may only add insignificantly to total budgets.

Accumulation of organic matter in deep-ocean sediments of the South Atlantic is related to primary productivity in the surface water. However, in many areas additional processes play a role. Varying remineralisation efficiencies in different regions strongly affect the amount of organic matter preserved in sediments. Little is known about the factors determining export and sequestration of carbon, which seems to vary in different oceanic environments. Along the continental margins, a strong control on organic matter sedimentation is exerted by current induced winnowing and focussing at morphologic depressions. These complex processes affecting organic carbon burial in sediments make it difficult to unambiguously estimate accumulation of organic matter and the related CO_2 fixation at a specific time. Transport of fine grained sediment particles including the organic fraction seems to be of major importance. This is illustrated by the asynchronous deposition of calcareous and organic material produced by marine planktic organisms on the continental margin off Southwest Africa. Continuous re-suspension of organic particles will lead to efficient diagenetic breakdown of organic compounds with CO_2 being released back into the active reservoirs. The point in time at which this occurs is dependent on how long organic matter remains in re-suspension loops, which in turn is probably controlled by current strength.

The observation of significant temporal offsets between marine organic biomarkers and calcareous sediment particles from identical sediment depth has important implications for multi-proxy paleoenvironmental studies. In order to compare records derived from different sediment fractions, confidence must exist in the precise age control of all parameters. If the assumption of synchronous deposition of the different sediment fractions proves to be wrong, these data cannot be directly compared, and apparent temporal leads or lags may be secondary signals. Furthermore, if fine-grained particles are transported over longer distances, the proxy data derived from the fine-grained fraction must be regarded as a regional, rather than a local signal. It must be assumed that the small grain size fraction consists of a mixture of allochthonous particles from various sources and with different absolute ages. Proxy data derived from such a mixture of particles will

be smoothed and signals are expected to be attenuated. High-frequency oscillations in climate have little preservation potential in these records.

Current induced winnowing and re-suspension has been shown to be common along continental slopes. The role of internal tides has only recently gained attention. Independent methods for the investigation of sediment redistribution, using heavy radioisotopes, combined with age comparison of co-occurring particles could add to the understanding of sedimentation processes. Further research of temporal relationships between the deposition of calcareous and organic particles at different settings will help in clarifying the role of currents, the importance of re-depositional processes, and the time required for final burial of organic matter on a global scale.

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